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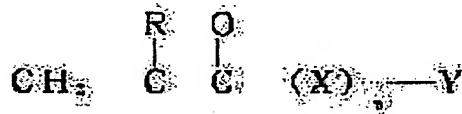
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(54) WATER-SWELLING RUBBER

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a water-swelling rubber containing a liquid-absorbing agent comprising the alkaline earth metal salt of a copolymer comprising an anionic monomer, etc., reduced in eluted components, high in the swelling ratio, excellent in durability and safety, and suitable as a water-stopping material for civil engineering works, etc.

SOLUTION: This water-swelling rubber contains a liquid-absorbing agent comprising the alkaline earth metal (e.g. magnesium) salt of a copolymer introduced from monomer components comprising (A) an anionic monomer such as (meth)acrylic acid and (B) a nonionic monomer of the formula [R is H, methyl; (X)_n are 2-4C oxyalkylene units containing oxyethylene units in a mole fraction of ≥50mol.% based on the whole oxyalkylene units; Y is a 1-5C alkoxy, phenoxy, etc.; n is 3-100]. The liquid-absorbing ratio of the liquid-absorbing material for an artificial sea water is preferably ≥5g/g.



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(54) 【発明の名称】 水膨潤性ゴム

(57) 【要約】

【課題】

膨潤倍率が高く、水道水等の清水または清水に近い水を吸収する場合における膨潤倍率と、塩類や多価金属イオン等を含有する硬水や海水、セメント水等の水性液体を吸収する場合における膨潤倍率との差が殆ど無く、しかも、水および水性液体に溶出する溶出成分(可溶成分)が従来よりも低減された水膨潤性ゴムを提供する。

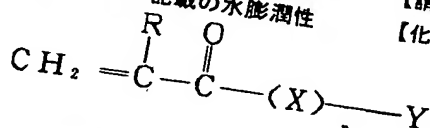
【解決手段】 水膨潤性ゴムは、人工海水に対する吸液倍率が5 g/g以上の吸液剤と、エラストマーとを含む。

該吸液剤は、例えば、アニオン性単量体のアルカリ土類金属塩と、ノニオン性単量体とを共重合させてなる。アニオン性単量体は、メタクリル酸が特に好ましい。ノニオン性単量体は、(メタ)アクリル酸エステル系単量体がより好ましく、メトキシポリエチレングリコールメタクリレートが特に好ましい。アルカリ土類金属は、マグネシウムがより好ましい。

【特許請求の範囲】

【請求項1】アニオン性単量体を含む単量体成分からなる吸液剤を含有する請求項1記載の水膨潤性ゴム。

【請求項2】人工海水に対する請求項1記載の水膨潤性ゴムの吸液剤の吸液倍率が5g/g以上であること。



..... (1)

(式中、Rは原子またはメチル基を表し、Xは全オキシアルキル基に対するオキシエチレン基のモル分率が50モル%以上である炭素数2~4のオキシアルキレン基を表し、Yは炭素数1~5のアルコキシ基、フェノキシ基、または置換基として炭素数1~9のアルキル基を平均66~100の整数を表す)で表される(メタ)アクリル酸エステル系単量体であることを特徴とする請求項1ないし3の何れか1項に記載の水膨潤性ゴム。

【請求項5】ノニオン性単量体がメトキシポリエチレングリコールメタクリレートであることを特徴とする請求項1ないし4の何れか1項に記載の水膨潤性ゴム。

【請求項6】アルカリ土類金属がマグネシウムであることを特徴とする請求項1ないし5の何れか1項に記載の水膨潤性ゴム。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、例えば、土木工事や建設工事等における止水材等として好適に供される水膨潤性ゴムに関するものである。

【0002】

【従来の技術】従来より、多価金属イオン等を含有する硬水や海水等の水性液体に対して、優れた耐塩性を示す吸液剤が知られている(特開平2-253845号公報)。この吸液剤(吸液剤)は、特定の構造を有する(メタ)アクリル酸エステル系単量体と、水溶性のカルボキシル基含有不飽和単量体とを架橋剤の存在下で共重合してなる架橋重合体からなっている。そして、該吸液剤は、上記の水性液体を吸収する吸液倍率に優れており、しかも、該吸液倍率が経時的に低下しないという特性を備えている。

【0003】

【発明が解決しようとする課題】しかしながら、上記従来の吸液剤を例えばエラストマーと混合して水膨潤性ゴムとして用いると、以下に示すような問題点を生じる。即ち、上記従来の吸液剤を含む水膨潤性ゴムは、水道水等の清水に近い水と接触した場合には大きく膨潤するが、セメント水等の多価金属イオンを多量に含有する水と接触した場合には少ししか膨潤しない。つまり、接触

ゴム。

【請求項3】上記吸液剤が、アニオン性単量体のアルカリ土類金属塩とノニオン性単量体とを共重合させてなることを特徴とする請求項1または2記載の水膨潤性ゴム。

【請求項4】ノニオン性単量体が一般式(1)

【化1】

する水の種類による膨潤倍率の差が大きいため、止水性能や耐久性に問題を残すものであった。

【0004】また、上記従来の吸液剤を含む水膨潤性ゴムは、水性液体と接触した場合に、比較的多量の溶出成分が溶出してくるために、安全性が高度に求められる用途分野での止水には、尚、問題が残るものであった。

【0005】本発明は、上記従来の問題点に鑑みなされ、その目的は、水道水等の清水または清水に近い水を吸収する場合における膨潤倍率と、塩類や多価金属イオン等を含有する硬水や海水、セメント水等の水性液体を吸収する場合における膨潤倍率との差が殆ど無く、しかも、水および水性液体に溶出する溶出成分が従来よりも低減された、止水性能、耐久性、および安全性に優れた水膨潤性ゴムを提供することにある。

【0006】

【課題を解決するための手段】本願発明者等は、上記の目的を達成すべく鋭意検討した結果、アニオン性単量体およびノニオン性単量体を含む単量体成分から導かれる共重合体のアルカリ土類金属塩からなる吸液剤を含む水膨潤性ゴムが、水道水等の清水または清水に近い水を吸収する場合における膨潤倍率と、塩類や多価金属イオン等を含有する硬水や海水、セメント水等の水性液体を吸収する場合における膨潤倍率との差が殆ど無く、しかも、水および水性液体に溶出する溶出成分(可溶成分)が従来よりも低減されることを見い出して、本発明を完成させるに至った。

【0007】即ち、請求項1記載の発明の水膨潤性ゴムは、上記の課題を解決するために、アニオン性単量体およびノニオン性単量体を含む単量体成分から導かれる共重合体のアルカリ土類金属塩からなる吸液剤を含むことを特徴としている。

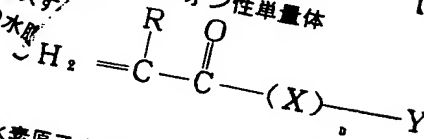
【0008】請求項2記載の発明の水膨潤性ゴムは、上記の課題を解決するために、請求項1記載の水膨潤性ゴムにおいて、人工海水に対する吸液剤の吸液倍率が5g/g以上であることを特徴としている。

【0009】請求項3記載の発明の水膨潤性ゴムは、上記の課題を解決するために、請求項1または2記載の水膨潤性ゴムにおいて、上記吸液剤が、アニオン性単量体のアルカリ土類金属塩とノニオン性単量体とを共重合させてなることを特徴とする請求項1または2記載の水膨潤性ゴム。

(3)

膨潤性ゴムは、上
【0010】請求項1ないし3の何れか
記の課題を解決す
1項に記載の水膨潤性ゴムは、上

が一般式(1)
【0011】
【化2】



Rは水素原子またはメチル基を表し、Xは、アルキレン基に対するオキシエチレン基のモル%以上である炭素数2~4のオキシアルキレン基、または置換基として炭素数1~9のアルキレン基を1~3個有するオキシアルキルフェニル基を表し、nは平均で3~100の整数を表す)で表される(メタ)アクリル酸エステル系単量体であることを特徴している。

【0013】請求項5記載の発明の水膨潤性ゴムは、上記の課題を解決するために、請求項1ないし4の何れか1項に記載の水膨潤性ゴムにおいて、ノニオン性単量体がメトキシポリエチレングリコールメタクリレートであることを特徴としている。

【0014】請求項6記載の発明の水膨潤性ゴムは、上記の課題を解決するために、請求項1ないし5の何れか1項に記載の水膨潤性ゴムにおいて、アルカリ土類金属がマグネシウムであることを特徴としている。

【0015】上記の構成によれば、水膨潤性ゴムに含まれる吸液剤は、アニオン性単量体およびノニオン性単量体を含む単量体成分から導かれる共重合体のアルカリ土類金属塩である。これにより、膨潤倍率が高く、水道水の清水または清水に近い水を吸収する場合における膨潤倍率と、塩類や多価金属イオン等を含有する硬水や海水、セメント水等の水性液体を吸収する場合における膨潤倍率との差が殆ど無く、しかも、水および水性液体に溶出する溶出成分(可溶成分)が従来よりも低減された水膨潤性ゴムを提供することができる。

【0016】以下に本発明を詳しく説明する。本発明における人工海水とは、脱イオン水に、硫酸カルシウム(CaSO₄)、硫酸マグネシウム(MgSO₄)、塩化マグネシウム(MgCl₂)、塩化カリウム(KCl)、および塩化ナトリウム(NaCl)を、調製すべき人工海水における濃度が、CaSO₄:1.38g/kg、MgSO₄:2.10g/kg、MgCl₂:3.32g/kg、KCl:0.72g/kg、NaCl:26.69g/kgとなるように溶解した水溶液を示す。

【0017】本発明にかかる水膨潤性ゴムは、吸液剤とエラストマーとを含んでいる。上記の吸液剤は、アニオン性単量体およびノニオン性単量体を含む単量体成分から導かれる共重合体のアルカリ土類金属塩である。上記アルカリ土類金属は、マグネシウムおよびカルシウム

がより好ましく、マグネシウムが特に好ましい。尚、上記の単量体成分は、アニオン性単量体およびノニオン性単量体以外の他の単量体を含んでもよい。

【0018】上記のアニオン性単量体は、後述の如くアルカリ土類金属と塩を形成可能な単量体であればよく、特に限定されるものではない。アニオン性単量体としては、具体的には、例えば、(メタ)アクリル酸、クロトン酸等の不飽和モノカルボン酸系単量体；マレイン酸、フマル酸、イタコン酸、シトラコン酸等の不飽和ジカルボン酸系単量体；ビニルスルホン酸、アリルスルホン酸、メタリルスルホン酸、ステレンスルホン酸、2-アクリルアミド-2-メチルプロパンスルホン酸、スルホエチレート、2-ヒドロキシスルホプロピル(メタ)アクリレート等の不飽和スルホン酸系単量体；(メタ)アクリルアミドメタンホスホン酸、2-(メタ)アクリルアミド-2-メチルプロパノホスホン酸等の不飽和ホスホン酸系単量体等が挙げられる。これらアニオン性単量体は、単独で用いてもよく、また、二種類以上を適宜混合して用いてもよい。上記例示の単量体のうち、不飽和モノカルボン酸系単量体がより好ましく、(メタ)アクリル酸がさらに好ましく、メタクリル酸が特に好ましい。

【0019】上記のノニオン性単量体は、アニオン性単量体と共重合可能な単量体であればよく、特に限定されるものではない。ノニオン性単量体としては、具体的に、例えば、前記一般式(1)で表される(メタ)アクリル酸エステル系単量体；2-ヒドロキシエチル(メタ)アクリレート、ポリエチレングリコールモノ(メタ)アクリレート、ポリプロピレングリコールモノ(メタ)アクリレート、アリルアルコール、ビニルアルコール等の水酸基含有不飽和単量体；(メタ)アクリルアミド、N-ビニルアセトアミド、ε-ブチル(メタ)アクリルアミド等のアミド系不飽和単量体；(メタ)アクリル酸エステル系不飽和単量体；エチレン、プロピレン、1-ブテン、メチル-1-ブテン(α-イソアミレン)、1-ヘキセン、1-ヘプテン等のα-オレフィン系単量体；アルコキシポリアルキレングリコールモノ(メタ)アクリレート等が挙げられる。また、上記の(メタ)アクリレート等が

%となるように両者を仕込んだ。また、ポリエチレングリコールジアクリレートを上記の単量体成分に対する割合が0.12モル%となるように仕込んだ。

【0069】次に、上記の反応液に窒素ガスを吹き込んで溶存酸素を追い出すと共に、反応系を窒素ガス置換した。続いて、水浴を用いて反応液の温度を50℃に昇温した後、10重量% 2,2'-アゾビス (2-アミジノプロパン) 塩酸塩水溶液1.21部を添加した。そして、該反応液を攪拌・混合した後、攪拌を停止した。すると、直ちに重合反応が開始された。2,2'-アゾビス (2-アミジノプロパン) 塩酸塩は、単量体成分に対する割合が0.15モル%となるように添加した。

【0070】上記の重合反応においては、反応を開始してから60分後に反応液の温度が58℃になり、ピークに達した。この間、水浴の温度は、反応液の温度とほぼ等しくなるように適宜昇温させた。反応液の温度がピークに達した後、水浴の温度を80℃に維持し、該反応液を60分間熟成した。反応終了後、得られた含水ゲル状重合体を取り出し、微粒子状に解砕した。

【0071】解砕した含水ゲル状重合体を、実施例1と同様にして乾燥・粉碎等することにより、60メッシュ～100メッシュの大きさの吸液剤を得た。得られた吸液剤の吸液倍率は51.3 g/gであった。この吸液剤を実施例1と同様にしてさらに粉碎して、平均粒子径が23μmである吸液剤粉末を得た。

【0072】次に、上記の吸液剤粉末を用いて実施例1と同様の操作を行ない、水膨潤性ゴムを得た。得られた水膨潤性ゴムの膨潤性および溶出性を測定した。結果を表1に記載した。

【0073】〔実施例6〕実施例5におけるポリエチレングリコールジアクリレートの使用量を0.17部から0.51部に変更した。つまり、ポリエチレングリコールジアクリレートを、単量体成分に対する割合が0.36モル%となるように仕込んだ以外は、実施例5と同様の反応および操作を行ない、吸液剤を得た。得られた吸液剤の吸液倍率は22.4 g/gであった。この吸液剤を実施例1と同様にしてさらに粉碎して、平均粒子径が18μmである吸液剤粉末を得た。

【0074】次に、上記の吸液剤粉末を用いて実施例1と同様の操作を行ない、水膨潤性ゴムを得た。得られた水膨潤性ゴムの膨潤性および溶出性を測定した。結果を表1に記載した。

【0075】〔実施例7〕実施例1と同様の反応器に、アニオン性単量体のアルカリ土類金属塩としての40重量%アクリル酸マグネシウム水溶液 100.2部、ノニオン性単量体としての40重量%アクリルアミド水溶液 199.8部、イオン交換水73.8部、および、架橋剤としての 1.5重量%N,N-メチレンビスアクリルアミド水溶液16.5部を仕込んで反応液とした。

【0076】つまり、アクリル酸マグネシウム水溶液中

のアクリル酸成分と、アクリルアミドとのモル比が、3:7となるようにすると共に、反応液における単量体成分の濃度が、30重量%となるように両者を仕込んだ。また、N,N-メチレンビスアクリルアミドを、上記の単量体成分に対する割合が 0.1モル%となるように仕込んだ。

【0077】次に、上記の反応液に窒素ガスを吹き込んで溶存酸素を追い出すと共に、反応系を窒素ガス置換した。続いて、水浴を用いて反応液の温度を20℃に昇温した後、重合開始剤としての10重量%過硫酸ナトリウム水溶液 (ラジカル発生剤) 4.88部および1重量%L-アスコルビン酸ナトリウム水溶液 (還元剤) 4.81部を添加した。そして、該反応液を攪拌・混合した後、攪拌を停止した。すると、直ちに重合反応が開始された。過硫酸ナトリウムは、単量体成分に対する割合が0.15モル%となるように添加した。また、L-アスコルビン酸ナトリウムは、単量体成分に対する割合が0.02モル%となるように添加した。

【0078】上記の重合反応においては、反応を開始してから3分後に反応液の温度が 108℃になり、ピークに達した。この間、水浴の温度は、90℃になるまで、反応液の温度とほぼ等しくなるように適宜昇温させた。反応液の温度がピークに達した後、水浴の温度を80℃に維持し、該反応液を30分間熟成した。反応終了後、得られた含水ゲル状重合体を取り出し、微粒子状に解砕した。

【0079】解砕した含水ゲル状重合体を、実施例1と同様にして乾燥・粉碎等することにより、60メッシュ～100メッシュの大きさの吸液剤を得た。得られた吸液剤の吸液倍率は24.6 g/gであった。この吸液剤を実施例1と同様にしてさらに粉碎して、平均粒子径が26μmである吸液剤粉末を得た。

【0080】次に、上記の吸液剤粉末を用いて実施例1と同様の操作を行ない、水膨潤性ゴムを得た。得られた水膨潤性ゴムの膨潤性および溶出性を測定した。結果を表1に記載した。

【0081】〔実施例8〕実施例1と同様の反応器に、40重量%アクリル酸マグネシウム水溶液 159部、メトキシポリエチレングリコールメタクリレート 176.4部、イオン交換水59.3部、および、ポリエチレングリコールジアクリレート0.65部を仕込んで反応液とした。上記のメトキシポリエチレングリコールメタクリレートにおけるエチレンオキシドの平均付加モル数は9モルである。また、ポリエチレングリコールジアクリレートにおけるエチレンオキシドの平均付加モル数は8モルである。

【0082】つまり、アクリル酸マグネシウム水溶液中のアクリル酸成分と、メトキシポリエチレングリコールメタクリレートとのモル比が、67:33となるようにすると共に、反応液における単量体成分の濃度が、60重量%となるように両者を仕込んだ。また、ポリエチレングリコールジアクリレートを、上記の単量体成分に対する割

合が0.12モル%となるように仕込んだ。

【0083】次に、上記の反応液に窒素ガスを吹き込んで溶存酸素を追い出すと共に、反応系を窒素ガス置換した。続いて、水浴を用いて反応液の温度を50℃に昇温した後、10重量% 2,2'-アゾビス (2-アミジノプロパン) 塩酸塩水溶液4.64部を添加した。そして、該反応液を攪拌・混合した後、攪拌を停止した。すると、直ちに重合反応が開始された。2,2'-アゾビス (2-アミジノプロパン) 塩酸塩は、単量体成分に対する割合が0.15モル%となるように添加した。

【0084】上記の重合反応においては、反応を開始してから49分後に反応液の温度が104℃になり、ピークに達した。この間、水浴の温度は、90℃になるまで、反応液の温度とほぼ等しくなるように適宜昇温させた。反応液の温度がピークに達した後、水浴の温度を80℃に維持し、該反応液を30分間熟成した。反応終了後、得られた含水ゲル状重合体を取り出し、微粒子状に解砕した。

【0085】解砕した含水ゲル状重合体を、実施例1と同様にして乾燥・粉碎等することにより、60メッシュ～100メッシュの大きさの吸液剤を得た。得られた吸液剤の吸液倍率は13.4 g/gであった。この吸液剤を実施例1と同様にしてさらに粉碎して、平均粒子径が25μmである吸液剤粉末を得た。

【0086】次に、上記の吸液剤粉末を用いて実施例1と同様の操作を行ない、水膨潤性ゴムを得た。得られた水膨潤性ゴムの膨潤性および溶出性を測定した。結果を表1に記載した。

【0087】〔比較例1〕実施例1におけるポリエチレングリコールジアクリレートの使用量を0.41部から8.2部に変更した。つまり、ポリエチレングリコールジアクリレートを、単量体成分に対する割合が3.0モル%となるように仕込んだ以外は、実施例1と同様の反応および操作を行ない、比較用の吸液剤を得た。得られた比較用の吸液剤の吸液倍率は3.8 g/gであった。この比較用の吸液剤を実施例1と同様にしてさらに粉碎して、平均粒子径が20μmである比較用の吸液剤粉末を得た。

【0088】次に、上記比較用の吸液剤粉末を用いて実施例1と同様の操作を行ない、比較用の水膨潤性ゴムを得た。得られた比較用の水膨潤性ゴムの膨潤性および溶出性を測定した。結果を表1に記載した。

【0089】〔比較例2〕実施例1と同様の反応器に、43重量%メタクリル酸ナトリウム水溶液178.0部、メトキシポリエチレングリコールメタクリレート163.4部、イオン交換水53.9部、および、ポリエチレングリコールジアクリレート0.25部を仕込んで反応液とした。上記のメトキシポリエチレングリコールメタクリレートにおけるエチレンオキシドの平均付加モル数は9モルである。また、ポリエチレングリコールジアクリレートにおけるエチレンオキシドの平均付加モル数は8モルである。

【0090】つまり、メタクリル酸ナトリウム水溶液中のメタクリル酸成分と、メトキシポリエチレングリコールメタクリレートとのモル比が、67:33となるように両者を仕込んだ。また、ポリエチレングリコールジアクリレートを、上記の単量体成分に対する割合が0.05モル%となるように仕込んだ。

【0091】次に、上記の反応液に窒素ガスを吹き込んで溶存酸素を追い出すと共に、反応系を窒素ガス置換した。続いて、水浴を用いて反応液の温度を40℃に昇温した後、10重量% 2,2'-アゾビス (2-アミジノプロパン) 塩酸塩水溶液4.3部を添加した。そして、該反応液を攪拌・混合した後、攪拌を停止した。すると、直ちに重合反応が開始された。2,2'-アゾビス (2-アミジノプロパン) 塩酸塩は、単量体成分に対する割合が0.15モル%となるように添加した。

【0092】上記の重合反応においては、反応を開始してから107分後に反応液の温度が88℃になり、ピークに達した。この間、水浴の温度は、反応液の温度とほぼ等しくなるように適宜昇温させた。反応液の温度がピークに達した後、水浴の温度を80℃に維持し、該反応液を60分間熟成した。反応終了後、得られた含水ゲル状重合体を取り出し、微粒子状に解砕した。

【0093】解砕した含水ゲル状重合体を、実施例1と同様にして乾燥・粉碎等することにより、60メッシュ～100メッシュの大きさの比較用の吸液剤を得た。得られた比較用の吸液剤の吸液倍率は21.8 g/gであった。この比較用の吸液剤を実施例1と同様にしてさらに粉碎して、平均粒子径が20μmである比較用の吸液剤粉末を得た。

【0094】次に、上記比較用の吸液剤粉末を用いて実施例1と同様の操作を行ない、比較用の水膨潤性ゴムを得た。得られた比較用の水膨潤性ゴムの膨潤性および溶出性を測定した。結果を表1に記載した。

【0095】〔比較例3〕実施例1と同様の反応器に、37重量%アクリル酸ナトリウム水溶液116.8部、40重量%アクリルアミド水溶液192部、イオン交換水64.5部、および、1.5重量%N,N-メチレンビスアクリルアミド水溶液15.8部を仕込んで反応液とした。

【0096】つまり、アクリル酸ナトリウム水溶液中のアクリル酸成分と、アクリルアミドとのモル比が、3:7となるようにすると共に、反応液における単量体成分の濃度が、30重量%となるように両者を仕込んだ。また、N,N-メチレンビスアクリルアミドを、上記の単量体成分に対する割合が0.1モル%となるように仕込んだ。

【0097】次に、上記の反応液に窒素ガスを吹き込んで溶存酸素を追い出すと共に、反応系を窒素ガス置換した。続いて、水浴を用いて反応液の温度を20℃に昇温した後、10重量%過硫酸ナトリウム水溶液5.5部および1重量%L-アスコルビン酸ナトリウム水溶液5.42部を添加した。そして、該反応液を攪拌・混合した後、攪拌を停

止した。すると、直ちに重合反応が開始された。過硫酸ナトリウムは、単量体成分に対する割合が0.15モル%となるように添加した。また、L-アスコルビン酸ナトリウムは、単量体成分に対する割合が0.02モル%となるように添加した。

【0098】上記の重合反応においては、反応を開始してから17分後に反応液の温度が108℃になり、ピークに達した。この間、水浴の温度は、90℃になるまで、反応液の温度とほぼ等しくなるように適宜昇温させた。反応液の温度がピークに達した後、水浴の温度を80℃に維持し、該反応液を30分間熟成した。反応終了後、得られた含水ゲル状重合体を取り出し、微粒子状に解砕した。

【0099】解砕した含水ゲル状重合体を、実施例1と同様にして乾燥・粉碎等することにより、60メッシュ～100メッシュの大きさの比較用の吸液剤を得た。得られた比較用の吸液剤の吸液倍率は21.7 g/gであった。この

比較用の吸液剤を実施例1と同様にしてさらに粉碎して、平均粒子径が $19\mu\text{m}$ である比較用の吸液剤粉末を得た。

【0100】次に、上記比較用の吸液剤粉末を用いて実施例1と同様の操作を行ない、比較用の水膨潤性ゴムを得た。得られた比較用の水膨潤性ゴムの膨潤性および溶出性を測定した。結果を表1に記載した。

【0101】〔比較例4〕実施例1における吸液剤粉末50部に代えて、市販のポリアクリル酸ナトリウム系の吸水性樹脂（株式会社日本触媒製；商品名 アクアリック K-4）50部を用いた以外は、実施例1と同様の操作を行ない、比較用の水膨潤性ゴムを得た。得られた比較用の水膨潤性ゴムの膨潤性および溶出性を測定した。結果を表1に記載した。

【0102】

【表1】

		吸液剤の 吸液倍率 (g/g)	水 膨 潤 性 ゴ ム の 性 能			
			膨 潤 性			溶 出 性
			膨潤倍率 (倍)		膨潤 倍率比	
			水道水	人工海水		
実 施 例	1	20.8	3.2	3.0	0.94	1.6
	2	23.3	3.3	3.0	0.91	1.8
	3	18.3	3.3	2.9	0.88	2.2
	4	5.5	2.4	2.2	0.92	1.6
	5	51.3	4.6	3.6	0.78	4.4
	6	22.4	3.3	2.8	0.85	3.8
	7	24.6	2.9	2.5	0.86	3.3
	8	13.4	2.6	2.4	0.92	2.8
比 較 例	1	3.8	1.8	1.7	0.94	1.6
	2	21.8	4.1	2.6	0.63	5.3
	3	21.7	3.7	2.5	0.68	6.3
	4	—	3.1	1.4	0.45	10.8

【0103】表1から明らかなように、本実施例にかかる水膨潤性ゴムは、水道水を吸収したときの膨潤倍率、および、人工海水を吸収したときの膨潤倍率が、共に2倍以上であり、かつ、膨潤倍率比が1に近い。これに対し、比較例1の比較用の水膨潤性ゴムは、吸液剤の吸液倍率が5 g/g未満であるため、膨潤倍率が共に2倍未満である。また、比較例2～比較例4の比較用の水膨潤性ゴムは、膨潤倍率比が1よりも極端に小さい。さらに、本実施例にかかる水膨潤性ゴムは、過マンガン酸カリウムの消費量が5 mg/l未満であるのに対し、比較例2～比較例4の比較用の水膨潤性ゴムは、該消費量が5 mg/l以上である。

【0104】つまり、実施例1～実施例8、および、比較例1～比較例4の結果から明らかなように、本実施例

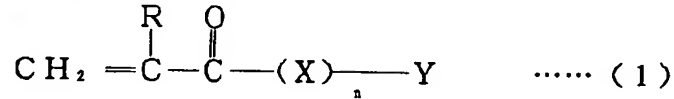
にかかる水膨潤性ゴムは、水道水を吸収したときの膨潤倍率、および、人工海水を吸収したときの膨潤倍率に優れていると共に、両膨潤倍率の差が殆ど無く、しかも、溶出成分（可溶成分）が比較用の水膨潤性ゴムよりも低減されていることがわかる。

【0105】

【発明の効果】本発明の請求項1記載の水膨潤性ゴムは、以上のように、アニオン性単量体およびノニオン性単量体を含む単量体成分から導かれる共重合体のアルカリ土類金属塩からなる吸液剤を含む構成である。

【0106】また、本発明の請求項2記載の水膨潤性ゴムは、以上のように、人工海水に対する吸液剤の吸液倍率が5 g/g以上である構成である。さらに、本発明の請求項3記載の水膨潤性ゴムは、以上のように、上記吸液

剤が、アニオン性単量体のアルカリ土類金属塩とノニオン性単量体とを共重合させてなる構成である。また、本発明の請求項 4 記載の水膨潤性ゴムは、以上のように、



【0108】(式中、Rは水素原子またはメチル基を表し、Xは全オキシアルキレン基に対するオキシエチレン基のモル分率が50モル%以上である炭素数2~4のオキシアルキレン基を表し、Yは炭素数1~5のアルコキシ基、フェノキシ基、または置換基として炭素数1~9のアルキル基を1~3個有するオキシアルキルフェニル基を表し、nは平均で3~100の整数を表す)で表される(メタ)アクリル酸エステル系単量体である構成である。さらに、本発明の請求項5記載の水膨潤性ゴムは、以上のように、ノニオン性単量体がメトキシポリエチレングリコールメタクリレートである構成である。また、

ノニオン性単量体が一般式(1)

【0107】

【化3】

本発明の請求項6記載の水膨潤性ゴムは、以上のように、アルカリ土類金属がマグネシウムである構成である。

【0109】これにより、膨潤倍率が高く、水道水等の清水または清水に近い水を吸収する場合における膨潤倍率と、塩類や多価金属イオン等を含有する硬水や海水、セメント水等の水性液体を吸収する場合における膨潤倍率との差が殆ど無く、しかも、水および水性液体に溶出する溶出成分(可溶成分)が従来よりも低減された水膨潤性ゴムを提供することができるという効果を奏する。

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CLAIMS

[Claim(s)]

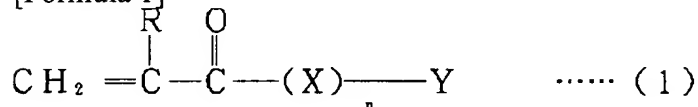
[Claim 1] Water bloating tendency rubber characterized by including the liquid absorption agent which consists of an alkaline-earth-metal salt of the copolymer led from the monomer component containing an anionic monomer and a nonionic monomer.

[Claim 2] Water bloating tendency rubber according to claim 1 characterized by the liquid absorption scale factor of the liquid absorption agent to artificial sea water being more than 5 g/g.

[Claim 3] Water bloating tendency rubber according to claim 1 or 2 to which the above-mentioned liquid absorption agent is characterized by coming to carry out copolymerization of the alkaline-earth-metal salt of an anionic monomer, and the nonionic monomer.

[Claim 4] A nonionic monomer is a general formula (1).

[Formula 1]



(R expresses a hydrogen atom or a methyl group among a formula, and X expresses the oxy-alkylene group of the carbon numbers 2-4 whose mole fractions of the oxyethylene radical to all oxy-alkylene groups are more than 50 mol %.) Y expresses the alkoxy group of carbon numbers 1-5, a phenoxy group, or the oxy-alkylphenyl radical that has 1-3 alkyl groups of carbon numbers 1-9 as a substituent. n -- an average -- the integer of 3-100 -- expressing -- water bloating tendency rubber given in claim 1 characterized by being the acrylic ester system monomer expressed (meta) thru/or any 1 term of 3.

[Claim 5] Water bloating tendency rubber given in claim 1 characterized by a nonionic monomer being methoxy polyethylene-glycol methacrylate thru/or any 1 term of 4.

[Claim 6] Water bloating tendency rubber given in claim 1 characterized by alkaline earth metal being magnesium thru/or any 1 term of 5.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the water bloating tendency rubber suitably offered as water cutoff material in a civil work, an construction work, etc.

[0002]

[Description of the Prior Art] The water absorption agent which shows the salt atmosphere which was excellent to aquosity liquids containing polyvalent metal ion etc., such as hard water and seawater, conventionally is known (JP,2-253845,A). This water absorption agent (liquid absorption agent) consists of cross linked polymer which comes to copolymerize the acrylic ester system monomer which has specific structure (meta), and a water-soluble carboxyl group content partial saturation monomer under existence of a cross linking agent. And this water absorption agent is excellent in the liquid absorption scale factor which absorbs the above-mentioned aquosity liquid, and, moreover, is equipped with the property that this liquid absorption scale factor does not fall with time.

[0003]

[Problem(s) to be Solved by the Invention] However, if the above-mentioned conventional water absorption agent is mixed with an elastomer and it uses as water bloating tendency rubber, a trouble as shown below will be produced. That is, the water bloating tendency rubber containing the above-mentioned conventional water absorption agent swells greatly, when the water near Shimizu, such as tap water, is contacted, but when the water which contains polyvalent metal ion, such as cement water, so much is contacted, it does not swell a few. That is, since the difference of the swelling scale factor by the class of water which contacts was large, it was what leaves a problem to the water cutoff engine performance and endurance.

[0004] Moreover, since comparatively a lot of leached moieties were eluted when an aquosity liquid is contacted, the water bloating tendency rubber containing the above-mentioned conventional water absorption agent was that by which a problem remains in water cutoff in the application field in which altitude is asked for safety in addition.

[0005] This invention is made in view of the above-mentioned conventional trouble. The purpose The swelling scale factor in the case of absorbing the water near Shimizu or Shimizu, such as tap water, There is almost no difference with the swelling scale factor in the case of absorbing aquosity liquids, such as hard water containing salts, polyvalent metal ion, etc., and seawater, cement water. And the leached moiety eluted into water and an aquosity liquid is to offer water bloating tendency rubber excellent in the water cutoff engine performance reduced conventionally, endurance, and safety.

[0006]

[Means for Solving the Problem] The water bloating tendency rubber containing the liquid absorption agent which consists of an alkaline-earth-metal salt of the copolymer led from the monomer component containing an anionic monomer and a nonionic monomer as a result of inquiring wholeheartedly that an invention-in-this-application person etc. should attain the above-mentioned purpose The swelling scale factor in the case of absorbing the water near Shimizu or Shimizu, such as tap water, There is almost no

difference with the swelling scale factor in the case of absorbing aqueous liquids, such as hard water containing salts, polyvalent metal ion, etc., and seawater, cement water, and it finds out that the leached moiety (meltable component) eluted into water and an aqueous liquid is moreover reduced conventionally, and came to complete this invention.

[0007] That is, the water bloating tendency rubber of invention according to claim 1 is characterized by including the liquid absorption agent which consists of an alkaline-earth-metal salt of the copolymer led from the monomer component containing an anionic monomer and a nonionic monomer, in order to solve the above-mentioned technical problem.

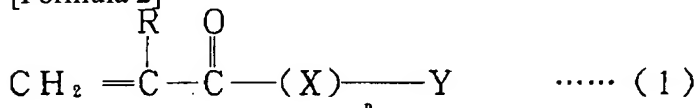
[0008] The water bloating tendency rubber of invention according to claim 2 is characterized by the liquid absorption scale factor of the liquid absorption agent to artificial sea water being more than 5 g/g in water bloating tendency rubber according to claim 1, in order to solve the above-mentioned technical problem.

[0009] In order that the water bloating tendency rubber of invention according to claim 3 may solve the above-mentioned technical problem, in water bloating tendency rubber according to claim 1 or 2, the above-mentioned liquid absorption agent is characterized by coming to carry out copolymerization of the alkaline-earth-metal salt of an anionic monomer, and the nonionic monomer.

[0010] For the water bloating tendency rubber of invention according to claim 4, in order to solve the above-mentioned technical problem, it sets to water bloating tendency rubber given in claim 1 thru/or any 1 term of 3, and a nonionic monomer is a general formula (1).

[0011]

[Formula 2]



[0012] (R expresses a hydrogen atom or a methyl group among a formula, and X expresses the oxy-alkylene group of the carbon numbers 2-4 whose mole fractions of the oxyethylene radical to all oxy-alkylene groups are more than 50 mol %.) Y expresses the alkoxy group of carbon numbers 1-5, a phenoxy group, or the oxy-alkylphenyl radical that has 1-3 alkyl groups of carbon numbers 1-9 as a substituent. n -- an average -- the integer of 3-100 -- expressing -- it is characterized by being the acrylic ester system monomer expressed (meta).

[0013] The water bloating tendency rubber of invention according to claim 5 is characterized by a nonionic monomer being methoxy polyethylene-glycol methacrylate in water bloating tendency rubber given in claim 1 thru/or any 1 term of 4, in order to solve the above-mentioned technical problem.

[0014] The water bloating tendency rubber of invention according to claim 6 is characterized by alkaline earth metal being magnesium in water bloating tendency rubber given in claim 1 thru/or any 1 term of 5, in order to solve the above-mentioned technical problem.

[0015] According to the above-mentioned configuration, the liquid absorption agent contained in water bloating tendency rubber is the alkaline-earth-metal salt of the copolymer led from the monomer component containing an anionic monomer and a nonionic monomer. Thereby, a swelling scale factor is high, there is almost no difference with the swelling scale factor in the case of absorbing aqueous liquids, such as hard water containing the swelling scale factor in the case of absorbing the water near Shimizu or Shimizu, such as tap water, salts, polyvalent metal ion, etc., and seawater, cement water, and, moreover, the water bloating tendency rubber with which the leached moiety (meltable component) eluted into water and an aqueous liquid was reduced conventionally can be offered.

[0016] This invention is explained in detail below. Artificial sea water in this invention shows the water solution with which it dissolves and it becomes deionized water as the concentration in artificial sea water which should prepare a calcium sulfate (CaSO₄), magnesium sulfate (MgSO₄), a magnesium chloride (MgCl₂), potassium chloride (KCl), and a sodium chloride (NaCl) serves as CaSO₄ 3.32 g/kg, KCl:0.72 g/kg, and NaCl:26.69 g/kg. : 1.38 g/kg, MgSO₄ : 2.10 g/kg, MgCl₂ :

[0017] The water bloating tendency rubber concerning this invention contains the liquid absorption

agent and the elastomer. The above-mentioned liquid absorption agent is the alkaline-earth-metal salt of the copolymer led from the monomer component containing an anionic monomer and a nonionic monomer. The above-mentioned alkaline earth metal has magnesium and more desirable calcium, and especially its magnesium is desirable. In addition, the above-mentioned monomer component may contain other monomers other than an anionic monomer and a nonionic monomer.

[0018] The above-mentioned anionic monomer is not especially limited like the after-mentioned that what is necessary is just the monomer which can form alkaline earth metal and a salt. As an anionic monomer, specifically For example, an acrylic acid (meta), Partial saturation monocarboxylic acid system monomers, such as a crotonic acid; A maleic acid, a fumaric acid, Partial saturation dicarboxylic acid system monomers, such as an itaconic acid and a citraconic acid; A vinyl sulfonic acid, An allyl compound sulfonic acid, a metallyl sulfonic acid, a styrene sulfonic acid, 2-acrylamide - isobutane sulfonic acid, Sulfoethyl (meta) acrylate, sulfopropyl (meta) acrylate, Partial saturation sulfonic-acid system monomers, such as 2-hydroxy sulfopropyl (meta) acrylate; (meta) acrylamide methane phosphonic acid, 2-(meta) acrylamide Partial saturation phosphonic acid system monomers, such as - isobutane phosphonic acid, etc. are mentioned. These anionic monomer may be used independently, and may mix two or more kinds suitably, and may be used. A partial saturation monocarboxylic acid system monomer is more desirable among the monomers of the above-mentioned instantiation, an acrylic acid (meta) is still more desirable, and especially a methacrylic acid is desirable.

[0019] The above-mentioned nonionic monomer is not limited especially that what is necessary is just as copolymerizable a monomer as an anionic monomer. The acrylic ester system monomer; 2-hydroxyethyl (meta) acrylate specifically expressed with said general formula (1) as a nonionic monomer (meta), Polyethylene-glycol monochrome (meta) acrylate, polypropylene-glycol monochrome (meta) acrylate, Hydroxyl-group content partial saturation monomers, such as allyl alcohol and vinyl alcohol; (meta) Acrylamide, Amide system partial saturation monomers, such as N-vinyl acetamide and t-butyl (meta) acrylamide; (meta) Acrylic ester, Nitril system partial saturation monomers [, such as hydrophobic partial saturation monomer; (meta) acrylonitrile], such as styrene, 2-methyl styrene, and vinyl acetate; Ethylene, A propylene, 1-butene, an isobutylene, alpha-amylene, 2-methyl -1-butene, 3-methyl Alpha olefin system monomers, such as -1-butene (alpha-iso amylene), 1-hexene, and 1-heptene; alkoxy polyalkylene glycol monochrome (meta) acrylate etc. is mentioned. moreover, as the above-mentioned acrylic ester (meta) system monomer Specifically For example, methoxy polyethylene-glycol monochrome (meta) acrylate, Butoxy polyethylene-glycol monochrome (meta) acrylate, methoxy polyethylene-glycol polypropylene-glycol monochrome (meta) acrylate, Methoxy polyethylene-glycol polybutylene glycol monochrome (meta) acrylate, Ethoxy polyethylene-glycol polypropylene-glycol monochrome (meta) acrylate, ethoxy polyethylene-glycol polybutylene glycol monochrome (meta) acrylate, etc. are mentioned. These nonionic monomer may be used independently, and may mix two or more kinds suitably, and may be used. The acrylic ester system monomer expressed with said general formula (1) among the monomers of the above-mentioned instantiation (meta) is more desirable, and especially methoxy polyethylene-glycol methacrylate is desirable. Moreover, when using methoxy polyethylene-glycol methacrylate as a nonionic monomer, the number of average addition mols of ethyleneoxide has desirable within the limits of five mols - 50 mols. That is, when Y is a methoxy group, within the limits of n of 5-50 is desirable [X in a general formula (1) is an oxyethylene radical, and R is a methyl group, and].

[0020] Although especially the rate of the anionic monomer in the above-mentioned the ratio of an anionic monomer and a nonionic monomer, i.e., copolymer component, is not limited, 5 % of the weight - 95% of the weight of its within the limits is more desirable, and 10 % of the weight - 70% of the weight of its within the limits is still more desirable. When there are few rates of an anionic monomer than 5 % of the weight, there is an inclination for the leached moiety in the copolymer obtained to increase. Moreover, when there are more rates of an anionic monomer than 95 % of the weight, the liquid absorption scale factor of a liquid absorption agent becomes low. Therefore, there is a possibility that water bloating tendency rubber equipped with the physical properties for which it asks may not be obtained.

[0021] The approach, i.e., the manufacture approach of a liquid absorption agent, of manufacturing the alkaline-earth-metal salt of the copolymer led from the monomer component containing an anionic monomer and a nonionic monomer After making for example, not the thing limited especially but ** anionic monomer, and chlorides, such as a calcium chloride and a magnesium chloride, react and forming the alkaline-earth-metal salt of an anionic monomer, The approach and ** anionic monomer to which copolymerization of the nonionic monomer is added and carried out, The approach and ** anionic monomer to which copolymerization of the nonionic monomer is added and carried out after making hydroxides, such as a calcium hydroxide and a magnesium hydroxide, react and forming the alkaline-earth-metal salt of an anionic monomer, After making carbonates, such as a calcium carbonate and a magnesium carbonate, react and forming the alkaline-earth-metal salt of an anionic monomer, After carrying out copolymerization of the approach and ** anionic monomer to which copolymerization of the nonionic monomer is added and carried out, and the nonionic monomer, After carrying out copolymerization of the approach and ** anionic monomer which add the above-mentioned chloride and form an alkaline-earth-metal salt, and the nonionic monomer, After carrying out copolymerization of the approach and ** anionic monomer which add the above-mentioned hydroxide and form an alkaline-earth-metal salt, and the nonionic monomer, various approaches, such as the approach of adding the above-mentioned carbonate and forming an alkaline-earth-metal salt, are employable. Moreover, after mixing an anionic monomer, a nonionic monomer, and a chloride, an above-mentioned hydroxide or an above-mentioned carbonate, copolymerization can be carried out and a liquid absorption agent can also be manufactured. The approach of ** and the approach of ** are more desirable among these approaches, and especially the approach of ** is desirable. Moreover, when adopting the approach of the above-mentioned **, especially a hydroxide has a desirable magnesium hydroxide. Since the solubility to water is large, the magnesium salt of an anionic monomer is suitable for a polymerization reaction.

[0022] Although the alkaline-earth-metal salt of the copolymer in the invention in this application is not clear about the reason whose leached moiety decreases compared with alkali-metal salts, such as sodium salt and potassium salt, it guesses as follows.

[0023] That is, it is guessed that it is for the solubility of a fusibility polymer to fall as a result of constructing a bridge over this fusibility polymer two-dimensional or in three dimensions with alkaline earth metal although a leached moiety uses a fusibility polymer as a principal component.

[0024] Well-known various approaches, for example, a solution polymerization method, a suspension-polymerization method, an opposition suspension-polymerization method, etc. can be conventionally used for a polymerization method. In addition, although especially the stirring approach at the time of performing a polymerization reaction is not limited, it is more desirable to stir subdividing the gel copolymer (it mentioning later) to generate according to this double arm mold kneader's shearing force using a double arm mold kneader as stirring equipment.

[0025] Although it is not limited, since low-temperature one becomes large, its molecular weight of a copolymer is comparatively desirable, and since a polymerization reaction completes especially reaction temperature, within the limits of 20 degrees C - 100 degree C is still more desirable [reaction temperature]. In addition, what is necessary is just to set up reaction time suitably according to the class (property) of reaction temperature, a monomer component, a polymerization initiator, a solvent, etc., etc., combination, the amount used, etc. so that the above-mentioned polymerization reaction may be completed.

[0026] A polymerization initiator can be used in case copolymerization of the monomer component is carried out. Specifically as this polymerization initiator, they are peroxides, such as a hydrogen peroxide, benzoyl peroxide, and cumene hydroperoxide.; Azo compounds, such as a 2 and 2'-azobisisobutyronitril, 2, 2'-azobis (2-amidinopropane) hydrochloride; radical generating agents (radical polymerization initiator), such as persulfate, such as ammonium persulfate, sodium persulfate, and potassium persulfate, etc. are mentioned. These polymerization initiators may be used independently, and may mix two or more kinds suitably, and may be used. Furthermore, the redox system initiator which comes to combine these radical generating agent and reducing agents, such as a sodium hydrogensulfite, and L-ascorbic acid (salt), ferrous salt, may be used. In addition, instead of using a

polymerization initiator, a radiation, an electron ray, ultraviolet rays, etc. may be irradiated, and a polymerization initiator and the exposure of these radiations, an electron ray, ultraviolet rays, etc., etc. may be used together.

[0027] Although especially the amount of the polymerization initiator used is not limited, 0.001 % of the weight - 10% of the weight of its within the limits is more desirable to a monomer component, and 0.01 % of the weight - 1% of the weight of its within the limits is still more desirable. Moreover, although especially the amount of the reducing agent used in the case of using a redox system initiator is not limited, its within the limits of 0.01-5 is more desirable to a radical generating agent at a weight ratio, and its within the limits of 0.05-2 is still more desirable.

[0028] Moreover, in case copolymerization of the monomer component is carried out, a cross linking agent may be used if needed. As this cross linking agent, specifically For example, a divinylbenzene, ethylene GURIKORUJI (meta) acrylate, Diethylene GURIKORUJI (meta) acrylate, TORIECHIRENGURIKORUJI (meta) acrylate, Propylene GURIKORUJI (meta) acrylate, polyethylene GURIKORUJI (meta) acrylate, TORIMECHI roll pro pantry (meta) acrylate, pen TAERISURITORUJI (meta) acrylate, Pen TAERISURITORUTORI (meta) acrylate, N, and N-methylenebis acrylamide, An isocyanuric acid triaryl, trimethylol propane diaryl ether, etc., The compound which has two or more ethylene system partial saturation radicals in 1 molecule; Ethylene glycol, A diethylene glycol, triethylene glycol, a polyethylene glycol, A glycerol, polyglycerin, propylene glycol, a polypropylene glycol, Polyvinyl alcohol, pentaerythritol, diethanolamine, Triethanolamine, sorbitol, sorbitan, a glucose, mannite, Polyhydric alcohol, such as Manni Tan, cane sugar, and grape sugar; Ethylene glycol diglycidyl ether, Polyethylene glycol diglycidyl ether, glycerol diglycidyl ether, Propylene glycol diglycidyl ether, polypropylene glycol diglycidyl ether, Neopentyl glycol diglycidyl ether, 1, 6-hexanediol diglycidyl ether, The Pori epoxy compounds, such as trimethylol propane diglycidyl ether, trimethylolpropane triglycidyl ether, and glycerol triglycidyl ether, etc. are mentioned. These cross linking agents may be used independently, and they may be mixed suitably and two or more kinds may be used for them.

[0029] By using a cross linking agent, the crosslinking density of a copolymer is controllable. What is necessary is not to limit especially the amount of the cross linking agent used, and just to set it up suitably by the class of the monomer component used or cross linking agent, the crosslinking density for which it asks. specifically, about 0.0005 to 0.02 within the limits has [the amount of the cross linking agent used] a more desirable mole ratio to a monomer component -- within the limits of 0.001-0.01 is still more desirable. In addition, when using polyhydric alcohol as a cross linking agent, they are after a polymerization reaction and a copolymer. It is desirable to heat-treat at 150 degrees C - 250 degree C. Moreover, when using the Pori epoxy compound as a cross linking agent, it is desirable after a polymerization reaction to heat-treat a copolymer at 50 degrees C - 250 degree C.

[0030] Furthermore, in case copolymerization of the monomer component is carried out, a solvent may be used if needed. Specifically as this solvent, aquosity solvents, such as a water; cyclohexane, a toluene; methanol, ethanol, an acetone, dimethylformamide, and dimethyl sulfoxide, etc. are mentioned. These solvents may be used independently, and may mix two or more kinds suitably, and may be used. Among the solvents of the above-mentioned instantiation, since safety can manufacture a liquid absorption agent still more highly and cheaply, the mixture of water and water, and an aquosity solvent has it. [more desirable] In addition, although especially the concentration of the monomer component in the case of using a solvent is not limited, 20 % of the weight - 80% of the weight of its within the limits is more desirable, and 30 % of the weight - 60% of the weight of its within the limits is still more desirable. While a polymerization reaction is easily controllable by making concentration of the monomer component in the solution containing this monomer component, a polymerization initiator, a cross linking agent, etc. into within the limits of the above, the yield of a copolymer can be raised and this copolymer can be obtained economically.

[0031] After a polymerization reaction, since it is obtained by gel, the alkaline-earth-metal salt of a copolymer dries the alkaline-earth-metal salt of this gel copolymer, after performing predetermined actuation of washing, a crack, etc. remaining as it is or if needed. Although especially drying

temperature is not limited, within the limits of 50 degrees C - 180 degree C being suitable and its within the limits which is 100 degree C to 170 degree C are the optimal. Moreover, after a dry matter operates grinding etc. and carries out grain refining, it performs classification actuation of sieving etc. if needed. Thereby, the liquid absorption agent more than 5 g/g is obtained for the liquid absorption scale factor to artificial sea water.

[0032] Moreover, in order to reduce a leached moiety and to raise the safety of this liquid absorption agent further by decreasing the unreacted monomer component which remains to a liquid absorption agent, it is desirable to use a reducing agent and to process the alkaline-earth-metal salt of a gel copolymer or its dry matter. Specifically as this reducing agent, a sodium sulfite, potassium sulfite, ammonium sulfite, a sodium hydrogensulfite, a potassium hydrogensulfite, hydrogen sulfite ammonium, a sodium thiosulfate, potassium thiosulfate, ammonium thiosulfate, L-ascorbic acid, ammonia, monoethanolamine, a glucose, etc. are mentioned. These reducing agents may be used independently, and may mix two or more kinds suitably, and may be used. A sodium sulfite, a sodium hydrogensulfite, and a sodium thiosulfate are more desirable among the reducing agents of the above-mentioned instantiation. although especially the amount of the reducing agent used is not limited, specifically, about 0.0001 to 0.02 within the limits has a more desirable mole ratio to the used monomer component - within the limits of 0.001-0.01 is still more desirable.

[0033] Although especially the configuration of a liquid absorption agent etc. is not limited, it is desirable that the mean particle diameter is 5 micrometers - about 70 micrometers, and it is more desirable that it is 10 micrometers - about 50 micrometers so that it can mix with an elastomer to homogeneity (distribution) and water bloating tendency rubber can swell in homogeneity. In addition, the above-mentioned mean particle diameter is volume mean particle diameter.

[0034] Especially the above-mentioned elastomer is not limited and well-known various compounds can be conventionally used for it. Specifically as this elastomer, they are polybutadiene rubber, polyisoprene rubber, styrene-butadiene copolymer rubber, chloroprene rubber, isoprene-isobutylene copolymer rubber, and ethylene. - It is alpha. - Ethylene, such as olefine copolymer rubber and ethylene propylene rubber (EPDM) rubber - alpha - Synthetic rubber, such as olefin-nonconjugated diene copolymer rubber; the synthetic-resin; natural rubber which has rubber elasticity, such as chlorinated polyethylene, chlorosulfonated polyethylene, an ethylene-vinylacetate copolymer, plasticized polyvinyl chloride, and polyurethane, is mentioned. These elastomers may be used independently, and may mix two or more kinds suitably, and may be used.

[0035] The rate of the liquid absorption agent and elastomer in water bloating tendency rubber, i.e., the weight ratio of a liquid absorption agent and an elastomer, has desirable within the limits of 5:95-50:50, and its within the limits of 15:85-40:60 is more desirable. When there are few weight ratios of a liquid absorption agent than the above-mentioned range (less than 5), since water bloating tendency rubber cannot fully swell, it is not desirable. Moreover, when there are more weight ratios of a liquid absorption agent than the above-mentioned range (50 is exceeded), since water bloating tendency rubber becomes weak and reinforcement falls, it is not desirable.

[0036] Although the especially manufacture approach of water bloating tendency rubber, i.e., the mixed (kneading) approach of a liquid absorption agent and an elastomer, is not limited, it is desirable to mix to homogeneity using the well-known mechanical technique with which manufacture of rubber goods of kneading using kneading machines, such as a roll mill and a Banbury mixer, etc. is presented conventionally. Moreover, what is necessary is just to fabricate this mixture in a predetermined configuration using the shaping approaches, such as extrusion molding and press forming, if needed. Thereby, water bloating tendency rubber is obtained.

[0037] As for water bloating tendency rubber, the additive other than a liquid absorption agent and an elastomer may be added if needed. As this additive, a vulcanizing agent, a vulcanization accelerator, a vulcanization assistant, an inorganic bulking agent, a reinforcing agent, a softener, a plasticizer, a coloring agent, an ultraviolet ray absorbent, lubricant, an antioxidant, etc. are mentioned, for example. These additives may be used independently, and may mix two or more kinds suitably, and may be used. the amount of the additive used -- the total quantity of a liquid absorption agent and an elastomer --

receiving -- for example, 100 or less % of the weight -- desirable -- Although it is good, it is not limited especially that what is necessary is just 0.1 % of the weight - 60% of the weight of within the limits, then the amount which does not spoil the physical properties (for example, reinforcement etc.) of water bloating tendency rubber. Moreover, especially the addition approach of an additive is not limited.

[0038] As the above-mentioned vulcanizing agent, although sulfur, flower of sulfur, deoxidation sulfur, precipitated sulfur, colloid sulfur, a sulfur chloride; zinc oxide, a magnesium oxide, a selenium, tellurium; peroxide; nitroaromatic, etc. are mentioned, specifically, it is not limited especially. These vulcanizing agents may be used independently, and may mix two or more kinds suitably, and may be used. As opposed to the total quantity of a liquid absorption agent and an elastomer, the amount of the vulcanizing agent used is not 0.1 % of the weight - 10% of the weight of within the limits, then the thing limited especially, although it is good.

[0039] As the above-mentioned vulcanization accelerator, although guanidine, aldehyde ammonia, aldehyde amines, a nitroso compound, thiazoles, thiazoline, imidazoline, thiourea, thio-acid salts, the Calvi thio-acid salts, iso thiourea salts, etc. are mentioned, specifically, it is not limited especially. These vulcanization accelerators may be used independently, and may mix two or more kinds suitably, and may be used. As opposed to the total quantity of a liquid absorption agent and an elastomer, the amount of the vulcanization accelerator used is not 0.1 % of the weight - 10% of the weight of within the limits, then the thing limited especially, although it is good.

[0040] As the above-mentioned vulcanization assistant, although a sodium hydroxide, a calcium oxide, a magnesium oxide (magnesia), a zinc white, lead(II) oxide, etc. are mentioned, specifically, it is not limited especially. These vulcanization assistant may be used independently, and may mix two or more kinds suitably, and may be used. As opposed to the total quantity of a liquid absorption agent and an elastomer, the amount of the vulcanization assistant used is not 0.1 % of the weight - 10% of the weight of within the limits, then the thing limited especially, although it is good.

[0041] Although what is necessary is just to heat-treat for [for / 1 minute / -] 30 minutes at 100 degree C to 200 degree C in case an elastomer is vulcanized, especially processing conditions are not limited. In addition, what is necessary is just to perform this heat-treatment after the time of shaping of the mixture which consists of a liquid absorption agent, an elastomer, etc., or shaping.

[0042] Moreover, as the above-mentioned inorganic bulking agent, although inorganic substances, such as a titanium dioxide, a calcium carbonate, a zinc white, clay, a kaolin, a bentonite, a silica, talc, a zeolite, and white carbon, are mentioned, specifically, it is not limited especially. These inorganic bulking agents may be used independently, and may mix two or more kinds suitably, and may be used. As opposed to the total quantity of a liquid absorption agent and an elastomer, the amount of the inorganic bulking agent used is not 10 % of the weight - 50% of the weight of within the limits, then the thing limited especially, although it is good.

[0043] The water bloating tendency rubber concerning this invention is a configuration containing the liquid absorption agent which consists of an alkaline-earth-metal salt of the copolymer led from the monomer component containing an anionic monomer and a nonionic monomer as mentioned above.

[0044] Moreover, water bloating tendency rubber is the configuration that the liquid absorption scale factor of the liquid absorption agent to artificial sea water is more than 5 g/g, as mentioned above. Furthermore, water bloating tendency rubber is a configuration to which the above-mentioned liquid absorption agent comes to carry out copolymerization of the alkaline-earth-metal salt of an anionic monomer, and the nonionic monomer as mentioned above. Moreover, water bloating tendency rubber is the configuration that a nonionic monomer is an acrylic ester system monomer expressed with said general formula (1) (meta), as mentioned above. Furthermore, water bloating tendency rubber is the configuration that a nonionic monomer is methoxy polyethylene-glycol methacrylate, as mentioned above. Moreover, water bloating tendency rubber is the configuration that alkaline earth metal is magnesium, as mentioned above.

[0045] Thereby, a swelling scale factor is high, there is almost no difference with the swelling scale factor in the case of absorbing aqueous liquids, such as hard water containing the swelling scale factor in the case of absorbing the water near Shimizu or Shimizu, such as tap water, salts, polyvalent metal

ion, etc., and seawater, cement water, and, moreover, the water bloating tendency rubber with which the leached moiety (melttable component) eluted into water and an aqueous liquid was reduced conventionally can be offered. Water bloating tendency rubber is suitably offered as the water cutoff material in civil works, construction works, etc., such as tunnel excavation, the water cutoff material of tap water, the exsorption prevention material which prevents the exsorption to the exterior of industrial waste water, etc. In addition, water bloating tendency rubber may be fabricated by predetermined configurations, such as a letter of a block.

[0046]

[Example] Hereafter, although an example and the example of a comparison explain this invention to a detail further, this invention is not limited at all by these. In addition, the engine performance of a liquid absorption agent and water bloating tendency rubber was measured by the following approaches. Moreover, the "section" given in an example and the example of a comparison shows the "weight section."

[0047] (a) About 1g of liquid absorption scale-factor liquid absorption agents of a liquid absorption agent was put into the tea bag type bag at homogeneity, and it was immersed all over artificial sea water. Weight W1 of a tea bag type bag after pulling up a tea bag type bag after 24-hour standing and performing a fixed time amount ridge (g) It measured. Moreover, same actuation is performed without using a liquid absorption agent, and it is the weight W0 of the tea bag type bag at that time (g). It measured. these weight W1 and W0 from -- weight of a degree type, and a liquid absorption scale-factor (g/g) = (weight W1 (g)-weight W0 (g)) / liquid absorption agent (g) -- following -- liquid absorption scale factor (g/g) It computed. [and] In addition, this liquid absorption scale factor is a balanced value.

[0048] (b) Cut off the bloating tendency water bloating tendency rubber of water bloating tendency rubber so that it may become 3mm in thickness on a 2cmx2cm square, and create a test piece, and it is the weight. (g) After measuring, this test piece was immersed all over tap water or artificial sea water. The weight after pulling up a test piece after standing for 30 days and wiping off moisture lightly through a filter paper (g) It measured. And the degree type from these weight and weight of the test piece after swelling scale-factor (twice) = immersion (g) The swelling scale factor (twice) was computed according to the weight (g) of the test piece before /immersion.

[0049] Moreover, it asked for the ratio (swelling scale factor when absorbing the swelling scale factor / tap water when absorbing artificial sea water) of the swelling scale factor when absorbing tap water, and the swelling scale factor when absorbing artificial sea water, and this value was made into the swelling scale-factor ratio.

[0050] (c) Elution nature JIS of water bloating tendency rubber K Based on the dissolution test judging approach of 6353 "the rubber for waterworks", the elution nature of water bloating tendency rubber was measured. First, it is water bloating tendency rubber the thickness of 3mm, and the surface area of 20cm² It cut off and the test piece was created so that it might become, and this test piece was immersed into deionized water 1L. This deionized water was extracted after 24-hour standing, and this was made into sample water. Moreover, same actuation was performed without immersing a test piece, and blank sample water was prepared. On the other hand, they are N / 100 potassium permanganate water solutions. N / 100 sodium-oxalate water solutions are prepared, and it is **. N / 100 sodium-oxalate water solutions are used. N / 100 potassium permanganate water solutions are titrated, and it is **. The factor of N / 100 potassium permanganate water solutions was computed.

[0051] subsequently -- this -- Above-mentioned sample water and blank sample water were titrated using N / 100 potassium permanganate water solutions. And according to the degree type, the consumption (mg/l) of potassium permanganate was computed and this value estimated the elution nature of water bloating tendency rubber.

[0052] $A = (a - b) - f \times (1000 / I) \times B$ -- however A : Consumption a of potassium permanganate (mg/l) : It required for sample water. Total quantity b of N / 100 potassium permanganate water solutions (ml) : It required for blank sample water. The total quantity (ml) f of N / 100 potassium permanganate water solutions : Factor I of N / 100 potassium permanganate water solutions : Amount B of sample water (ml) : It is 0.316 (mg/l).

[0053] [Example 1] Content volume equipped with a thermometer, nitrogen gas installation tubing, and an agitator To the 600ml reactor made from plastics, it is a 35-% of the weight methacrylic-acid magnesium water solution as an alkaline-earth-metal salt of an anionic monomer. The 203 sections, methoxy polyethylene-glycol methacrylate as a nonionic monomer The 169 sections, the ion-exchange-water 23.2 section as a solvent, and the polyethylene-glycol diacrylate 0.41 section as a cross linking agent were taught, and it considered as reaction mixture. The number of average addition mols of the ethyleneoxide in the above-mentioned methoxy polyethylene-glycol methacrylate is nine mols. Moreover, the number of average addition mols of the ethyleneoxide in polyethylene-glycol diacrylate is eight mols.

[0054] That is, both were taught so that the concentration of the sum total of the above-mentioned methacrylic-acid component and methoxy polyethylene-glycol methacrylate in reaction mixture, i.e., the concentration of a monomer component, might become 60 % of the weight, while making it the mole ratio of the methacrylic-acid component in a methacrylic-acid magnesium water solution and methoxy polyethylene-glycol methacrylate set to 67:33. Moreover, polyethylene-glycol diacrylate was taught so that the rate to the above-mentioned monomer component might become 0.12-mol %.

[0055] Next, while blowing nitrogen gas into the above-mentioned reaction mixture and driving out dissolved oxygen, nitrogen inert gas replacement of the system of reaction was carried out. Then, 10 % of the weight as a polymerization initiator after carrying out the temperature up of the temperature of reaction mixture to 40 degrees C using a water bath The 2 and 2'-azobis (2-amidinopropane) hydrochloride (Wako Pure Chem Industries make; trade name V-50) water-solution 4.44 section was added. And stirring was stopped after stirring and mixing this reaction mixture. Then, the polymerization reaction was started immediately. The 2 and 2'-azobis (2-amidinopropane) hydrochloride was added so that the rate to a monomer component might become 0.15-mol %.

[0056] In the above-mentioned polymerization reaction, 38 minutes after starting the reaction, the temperature of reaction mixture became 93 degrees C, and reached the peak. In the meantime, the temperature up of the temperature of a water bath was suitably carried out so that it might become almost equal to the temperature of reaction mixture. After the temperature of reaction mixture reached the peak, the temperature of a water bath was maintained at 80 degrees C, and this reaction mixture was riped for 30 minutes. The obtained water gel polymer was taken out after reaction termination, and it cracked in the shape of a particle.

[0057] After drying the cracked water gel polymer at the bottom of a nitrogen air current, and 150 degree C for 1 hour using a hot blast circulation type dryer, the liquid absorption agent of the magnitude of 60 meshes - 100 meshes was obtained by grinding a dry matter using a table-top-type grinder, and classifying at a wire gauze etc. further.

[0058] The liquid absorption scale factor of the obtained liquid absorption agent was measured by the above-mentioned approach. Consequently, the liquid absorption scale factor was 20.8 g/g. It ground further and liquid absorption agent powder was obtained so that mean particle diameter might be set to 15 micrometers using a jet mill in this liquid absorption agent.

[0059] Next, chloroprene rubber as an elastomer In the 100 sections, the magnesium-oxide 4 section as the liquid absorption agent powder 50 section, an above-mentioned vulcanizing agent, and an above-mentioned vulcanization assistant, the zinc-oxide 5 section as a vulcanizing agent, the vulcanization-accelerator 1 section, the lubricant 1 section, the antioxidant 2 section, the calcium-carbonate 20 section as an inorganic bulking agent, and the softener 15 section were mixed. And thickness after kneading this mixture for 20 minutes using a 10 inch trial mill The compound was obtained by extending to 3.5mm. Subsequently, an electric heat press machine is used for the above-mentioned compound. By vulcanizing for 10 minutes at 170 degrees C, the water bloating tendency rubber of the shape of a sheet with a thickness of 3mm was obtained.

[0060] The bloating tendency and elution nature of water bloating tendency rubber which were obtained were measured by the above-mentioned approach. Consequently, swelling scale factor when absorbing tap water Swelling scale factor when being 3.2 times and absorbing artificial sea water It was 3.0 times and the swelling scale-factor ratio was 0.94. Moreover, consumption of potassium permanganate It was

1.6 mg/l. These results were indicated to Table 1.

[0061] [Example 2] Methoxy polyethylene-glycol methacrylate in an example 1 whose number of average addition mols of ethyleneoxide is nine mols Methoxy polyethylene-glycol methacrylate whose number of average addition mols of ethyleneoxide it replaces with the 169 sections and is 50 mols (nonionic monomer) Except having used the 169 sections, the same reaction and actuation as an example 1 were performed, and the liquid absorption agent was obtained. The liquid absorption scale factor of the obtained liquid absorption agent was 23.3 g/g. This liquid absorption agent was further ground like the example 1, and the liquid absorption agent powder whose mean particle diameter is 32 micrometers was obtained.

[0062] Next, the same actuation as an example 1 was performed using the above-mentioned liquid absorption agent powder, and water bloating tendency rubber was obtained. The bloating tendency and elution nature of water bloating tendency rubber which were obtained were measured. The result was indicated to Table 1.

[0063] [Example 3] Methoxy polyethylene-glycol methacrylate in an example 1 Butoxy polyethylene-glycol methacrylate whose number of average addition mols of ethyleneoxide it replaces with the 169 sections and is 80 mols (nonionic monomer) Except having used the 169 sections, the same reaction and actuation as an example 1 were performed, and the liquid absorption agent was obtained. The liquid absorption scale factor of the obtained liquid absorption agent was 18.3 g/g. This liquid absorption agent was further ground like the example 1, and the liquid absorption agent powder whose mean particle diameter is 74 micrometers was obtained.

[0064] Next, the same actuation as an example 1 was performed using the above-mentioned liquid absorption agent powder, and water bloating tendency rubber was obtained. The bloating tendency and elution nature of water bloating tendency rubber which were obtained were measured. The result was indicated to Table 1.

[0065] [Example 4] It is from the 0.41 sections about the amount of the polyethylene-glycol diacrylate used in an example 1. It changed into the 4.1 sections. That is, the rate to a monomer component polyethylene-glycol diacrylate Except having taught so that it might become 1.5-mol %, the same reaction and actuation as an example 1 were performed, and the liquid absorption agent was obtained. Liquid absorption scale factor of the obtained liquid absorption agent It was 5.5 g/g. This liquid absorption agent was further ground like the example 1, and the liquid absorption agent powder whose mean particle diameter is 7 micrometers was obtained.

[0066] Next, the same actuation as an example 1 was performed using the above-mentioned liquid absorption agent powder, and water bloating tendency rubber was obtained. The bloating tendency and elution nature of water bloating tendency rubber which were obtained were measured. The result was indicated to Table 1.

[0067] [Example 5] To the same reactor as an example 1, it is a 10-% of the weight methacrylic-acid calcium water solution as an alkaline-earth-metal salt of an anionic monomer. The 313 sections, the methoxy polyethylene-glycol methacrylate 68.7 section, the ion-exchange-water 16.9 section, and the polyethylene-glycol diacrylate 0.17 section were taught, and it considered as reaction mixture. The number of average addition mols of the ethyleneoxide in the above-mentioned methoxy polyethylene-glycol methacrylate is nine mols. Moreover, the number of average addition mols of the ethyleneoxide in polyethylene-glycol diacrylate is eight mols.

[0068] That is, both were taught so that the concentration of the methacrylic-acid component in a methacrylic-acid calcium water solution and the monomer component in reaction mixture while making it a mole ratio with methoxy polyethylene-glycol methacrylate set to 67:33 might become 25 % of the weight. Moreover, polyethylene-glycol diacrylate was taught so that the rate to the above-mentioned monomer component might become 0.12-mol %.

[0069] Next, while blowing nitrogen gas into the above-mentioned reaction mixture and driving out dissolved oxygen, nitrogen inert gas replacement of the system of reaction was carried out. Then, 10 % of the weight after carrying out the temperature up of the temperature of reaction mixture to 50 degrees C using a water bath The 2 and 2'-azobis (2-amidinopropane) hydrochloride water-solution 1.21 section

was added. And stirring was stopped after stirring and mixing this reaction mixture. Then, the polymerization reaction was started immediately. The 2 and 2'-azobis (2-amidinopropane) hydrochloride was added so that the rate to a monomer component might become 0.15-mol %.

[0070] In the above-mentioned polymerization reaction, 60 minutes after starting the reaction, the temperature of reaction mixture became 58 degrees C, and reached the peak. In the meantime, the temperature up of the temperature of a water bath was suitably carried out so that it might become almost equal to the temperature of reaction mixture. After the temperature of reaction mixture reached the peak, the temperature of a water bath was maintained at 80 degrees C, and this reaction mixture was riped for 60 minutes. The obtained water gel polymer was taken out after reaction termination, and it cracked in the shape of a particle.

[0071] When desiccation, grinding, etc. made the cracked water gel polymer be the same as that of an example 1, the liquid absorption agent of the magnitude of 60 meshes - 100 meshes was obtained. The liquid absorption scale factor of the obtained liquid absorption agent was 51.3 g/g. This liquid absorption agent was further ground like the example 1, and the liquid absorption agent powder whose mean particle diameter is 23 micrometers was obtained.

[0072] Next, the same actuation as an example 1 was performed using the above-mentioned liquid absorption agent powder, and water bloating tendency rubber was obtained. The bloating tendency and elution nature of water bloating tendency rubber which were obtained were measured. The result was indicated to Table 1.

[0073] [Example 6] The amount of the polyethylene-glycol diacrylate used in an example 5 was changed into the 0.51 sections from the 0.17 sections. That is, except having taught polyethylene-glycol diacrylate so that the rate to a monomer component might become 0.36-mol %, the same reaction and actuation as an example 5 were performed, and the liquid absorption agent was obtained. The liquid absorption scale factor of the obtained liquid absorption agent was 22.4 g/g. This liquid absorption agent was further ground like the example 1, and the liquid absorption agent powder whose mean particle diameter is 18 micrometers was obtained.

[0074] Next, the same actuation as an example 1 was performed using the above-mentioned liquid absorption agent powder, and water bloating tendency rubber was obtained. The bloating tendency and elution nature of water bloating tendency rubber which were obtained were measured. The result was indicated to Table 1.

[0075] [Example 7] To the same reactor as an example 1, it is a 40-% of the weight acrylic-acid magnesium water solution as an alkaline-earth-metal salt of an anionic monomer. The 100.2 sections; 40-% of the weight acrylamide water solution as a nonionic monomer As the 199.8 sections, the ion-exchange-water 73.8 section, and a cross linking agent The 1.5-% of the weight N and N-methylenebis acrylamide water-solution 16.5 section was taught, and it considered as reaction mixture.

[0076] That is, both were taught so that the concentration of the acrylic-acid component in an acrylic-acid magnesium water solution and the monomer component in reaction mixture while making it a mole ratio with acrylamide set to 3:7 might become 30 % of the weight. Moreover, the rate to the above-mentioned monomer component N and N-methylenebis acrylamide It taught so that it might become 0.1-mol %.

[0077] Next, while blowing nitrogen gas into the above-mentioned reaction mixture and driving out dissolved oxygen, nitrogen inert gas replacement of the system of reaction was carried out. Then, after carrying out the temperature up of the temperature of reaction mixture to 20 degrees C using a water bath, the 10-% of the weight sodium persulfate water-solution (radical generating agent) 4.88 as a polymerization initiator section and the 1-% of the weight sodium L-ascorbate water-solution (reducing agent) 4.81 section were added. And stirring was stopped after stirring and mixing this reaction mixture. Then, the polymerization reaction was started immediately. Sodium persulfate was added so that the rate to a monomer component might become 0.15-mol %. Moreover, sodium L-ascorbate was added so that the rate to a monomer component might become 0.02-mol %.

[0078] In the above-mentioned polymerization reaction, 3 minutes after starting a reaction, the temperature of reaction mixture It became 108 degrees C and the peak was reached. In the meantime,

the temperature up of the temperature of a water bath was suitably carried out so that it might become almost equal to the temperature of reaction mixture, until it became 90 degrees C. After the temperature of reaction mixture reached the peak, the temperature of a water bath was maintained at 80 degrees C, and this reaction mixture was riped for 30 minutes. The obtained water gel polymer was taken out after reaction termination, and it cracked in the shape of a particle.

[0079] When desiccation, grinding, etc. made the cracked water gel polymer be the same as that of an example 1, the liquid absorption agent of the magnitude of 60 meshes - 100 meshes was obtained. The liquid absorption scale factor of the obtained liquid absorption agent was 24.6 g/g. This liquid absorption agent was further ground like the example 1, and the liquid absorption agent powder whose mean particle diameter is 26 micrometers was obtained.

[0080] Next, the same actuation as an example 1 was performed using the above-mentioned liquid absorption agent powder, and water bloating tendency rubber was obtained. The bloating tendency and elution nature of water bloating tendency rubber which were obtained were measured. The result was indicated to Table 1.

[0081] [Example 8] To the same reactor as an example 1, it is a 40-% of the weight acrylic-acid magnesium water solution. The 159 sections, methoxy polyethylene-glycol methacrylate The 176.4 sections, the ion-exchange-water 59.3 section, and the polyethylene-glycol diacrylate 0.65 section were taught, and it considered as reaction mixture. The number of average addition mols of the ethyleneoxide in the above-mentioned methoxy polyethylene-glycol methacrylate is nine mols. Moreover, the number of average addition mols of the ethyleneoxide in polyethylene-glycol diacrylate is eight mols.

[0082] That is, both were taught so that the concentration of the acrylic-acid component in an acrylic-acid magnesium water solution and the monomer component in reaction mixture while making it a mole ratio with methoxy polyethylene-glycol methacrylate set to 67:33 might become 60 % of the weight. Moreover, polyethylene-glycol diacrylate was taught so that the rate to the above-mentioned monomer component might become 0.12-mol %.

[0083] Next, while blowing nitrogen gas into the above-mentioned reaction mixture and driving out dissolved oxygen, nitrogen inert gas replacement of the system of reaction was carried out. Then, 10 % of the weight after carrying out the temperature up of the temperature of reaction mixture to 50 degrees C using a water bath The 2 and 2'-azobis (2-amidinopropane) hydrochloride water-solution 4.64 section was added. And stirring was stopped after stirring and mixing this reaction mixture. Then, the polymerization reaction was started immediately. The 2 and 2'-azobis (2-amidinopropane) hydrochloride was added so that the rate to a monomer component might become 0.15-mol %.

[0084] In the above-mentioned polymerization reaction, 49 minutes after starting a reaction, the temperature of reaction mixture It became 104 degrees C and the peak was reached. In the meantime, the temperature up of the temperature of a water bath was suitably carried out so that it might become almost equal to the temperature of reaction mixture, until it became 90 degrees C. After the temperature of reaction mixture reached the peak, the temperature of a water bath was maintained at 80 degrees C, and this reaction mixture was riped for 30 minutes. The obtained water gel polymer was taken out after reaction termination, and it cracked in the shape of a particle.

[0085] When desiccation, grinding, etc. made the cracked water gel polymer be the same as that of an example 1, the liquid absorption agent of the magnitude of 60 meshes - 100 meshes was obtained. The liquid absorption scale factor of the obtained liquid absorption agent was 13.4 g/g. This liquid absorption agent was further ground like the example 1, and the liquid absorption agent powder whose mean particle diameter is 25 micrometers was obtained.

[0086] Next, the same actuation as an example 1 was performed using the above-mentioned liquid absorption agent powder, and water bloating tendency rubber was obtained. The bloating tendency and elution nature of water bloating tendency rubber which were obtained were measured. The result was indicated to Table 1.

[0087] [Example 1 of a comparison] It is from the 0.41 sections about the amount of the polyethylene-glycol diacrylate used in an example 1. It changed into the 8.2 sections. That is, the rate to a monomer component polyethylene-glycol diacrylate Except having taught so that it might become 3.0-mol %, the

same reaction and actuation as an example 1 were performed, and the liquid absorption agent for a comparison was obtained. Liquid absorption scale factor of the obtained liquid absorption agent for a comparison It was 3.8 g/g. The liquid absorption agent for this comparison was further ground like the example 1, and the liquid absorption agent powder for a comparison whose mean particle diameter is 20 micrometers was obtained.

[0088] Next, the same actuation as an example 1 was performed using the liquid absorption agent powder for the above-mentioned comparison, and the water bloating tendency rubber for a comparison was obtained. The bloating tendency and elution nature of water bloating tendency rubber for a comparison which were obtained were measured. The result was indicated to Table 1.

[0089] [Example 2 of a comparison] To the same reactor as an example 1, it is a 43-% of the weight sodium methacrylate water solution. The 178.0 sections, methoxy polyethylene-glycol methacrylate The 163.4 sections, the ion-exchange-water 53.9 section, and the polyethylene-glycol diacrylate 0.25 section were taught, and it considered as reaction mixture. The number of average addition mols of the ethyleneoxide in the above-mentioned methoxy polyethylene-glycol methacrylate is nine mols. Moreover, the number of average addition mols of the ethyleneoxide in polyethylene-glycol diacrylate is eight mols.

[0090] That is, the mole ratio of the methacrylic-acid component in a sodium methacrylate water solution and methoxy polyethylene-glycol methacrylate taught both so that it might be set to 67:33. Moreover, polyethylene-glycol diacrylate was taught so that the rate to the above-mentioned monomer component might become 0.05-mol %.

[0091] Next, while blowing nitrogen gas into the above-mentioned reaction mixture and driving out dissolved oxygen, nitrogen inert gas replacement of the system of reaction was carried out. Then, 10 % of the weight after carrying out the temperature up of the temperature of reaction mixture to 40 degrees C using a water bath 2 and 2'-azobis (2-amidinopropane) hydrochloride water solution The 4.3 sections were added. And stirring was stopped after stirring and mixing this reaction mixture. Then, the polymerization reaction was started immediately. The 2 and 2'-azobis (2-amidinopropane) hydrochloride was added so that the rate to a monomer component might become 0.15-mol %.

[0092] Since a reaction is started in the above-mentioned polymerization reaction The temperature of reaction mixture became 88 degrees C after 107 minutes, and the peak was reached. In the meantime, the temperature up of the temperature of a water bath was suitably carried out so that it might become almost equal to the temperature of reaction mixture. After the temperature of reaction mixture reached the peak, the temperature of a water bath was maintained at 80 degrees C, and this reaction mixture was riped for 60 minutes. The obtained water gel polymer was taken out after reaction termination, and it cracked in the shape of a particle.

[0093] When desiccation, grinding, etc. made the cracked water gel polymer be the same as that of an example 1, the liquid absorption agent for the comparison of the magnitude of 60 meshes - 100 meshes was obtained. The liquid absorption scale factor of the obtained liquid absorption agent for a comparison was 21.8 g/g. The liquid absorption agent for this comparison was further ground like the example 1, and the liquid absorption agent powder for a comparison whose mean particle diameter is 20 micrometers was obtained.

[0094] Next, the same actuation as an example 1 was performed using the liquid absorption agent powder for the above-mentioned comparison, and the water bloating tendency rubber for a comparison was obtained. The bloating tendency and elution nature of water bloating tendency rubber for a comparison which were obtained were measured. The result was indicated to Table 1.

[0095] [Example 3 of a comparison] To the same reactor as an example 1, it is a 37-% of the weight acrylic-acid sodium water solution. The 116.8 sections, 40-% of the weight acrylamide water solution The 192 sections, ion-exchange-water 64.5 section and 1.5-% of the weight N, and N-methylenebis acrylamide water-solution 15.8 section was taught, and it considered as reaction mixture.

[0096] That is, both were taught so that the concentration of the acrylic-acid component in an acrylic-acid sodium water solution and the monomer component in reaction mixture while making it a mole ratio with acrylamide set to 3:7 might become 30 % of the weight. Moreover, the rate to the above-

mentioned monomer component N and N-methylenebis acrylamide It taught so that it might become 0.1-mol %.

[0097] Next, while blowing nitrogen gas into the above-mentioned reaction mixture and driving out dissolved oxygen, nitrogen inert gas replacement of the system of reaction was carried out. Then, 10-% of the weight sodium persulfate water solution after carrying out the temperature up of the temperature of reaction mixture to 20 degrees C using a water bath The 5.5 sections and the 1-% of the weight sodium L-ascorbate water-solution 5.42 section were added. And stirring was stopped after stirring and mixing this reaction mixture. Then, the polymerization reaction was started immediately. Sodium persulfate was added so that the rate to a monomer component might become 0.15-mol %. Moreover, sodium L-ascorbate was added so that the rate to a monomer component might become 0.02-mol %.

[0098] In the above-mentioned polymerization reaction, 17 minutes after starting a reaction, the temperature of reaction mixture It became 108 degrees C and the peak was reached. In the meantime, the temperature up of the temperature of a water bath was suitably carried out so that it might become almost equal to the temperature of reaction mixture, until it became 90 degrees C. After the temperature of reaction mixture reached the peak, the temperature of a water bath was maintained at 80 degrees C, and this reaction mixture was riped for 30 minutes. The obtained water gel polymer was taken out after reaction termination, and it cracked in the shape of a particle.

[0099] When desiccation, grinding, etc. made the cracked water gel polymer be the same as that of an example 1, the liquid absorption agent for the comparison of the magnitude of 60 meshes - 100 meshes was obtained. The liquid absorption scale factor of the obtained liquid absorption agent for a comparison was 21.7 g/g. The liquid absorption agent for this comparison was further ground like the example 1, and the liquid absorption agent powder for a comparison whose mean particle diameter is 19 micrometers was obtained.

[0100] Next, the same actuation as an example 1 was performed using the liquid absorption agent powder for the above-mentioned comparison, and the water bloating tendency rubber for a comparison was obtained. The bloating tendency and elution nature of water bloating tendency rubber for a comparison which were obtained were measured. The result was indicated to Table 1.

[0101] [Example 4 of a comparison] It replaced with the liquid absorption agent powder 50 section in an example 1, and except having used the absorptivity resin (NIPPON SHOKUBAI Make; trade name AKUA rucksack K-4) 50 section of a commercial sodium polyacrylate system, the same actuation as an example 1 was performed, and the water bloating tendency rubber for a comparison was obtained. The bloating tendency and elution nature of water bloating tendency rubber for a comparison which were obtained were measured. The result was indicated to Table 1.

[0102]

[Table 1]

		吸液剤の 吸液倍率 (g/g)	水 膨 潤 性 ゴ ム の 性 能			
			膨 潤 性			溶 出 性
			膨潤倍率 (倍)		膨潤 倍率比	過マンガン酸 カリウムの消 費量 (mg/l)
			水道水	人工海水		
実 施 例	1	20.8	3.2	3.0	0.94	1.6
	2	23.3	3.3	3.0	0.91	1.8
	3	18.3	3.3	2.9	0.88	2.2
	4	5.5	2.4	2.2	0.92	1.6
	5	51.3	4.6	3.6	0.78	4.4
	6	22.4	3.3	2.8	0.85	3.8
	7	24.6	2.9	2.5	0.86	3.3
	8	13.4	2.6	2.4	0.92	2.8
比 較 例	1	3.8	1.8	1.7	0.94	1.6
	2	21.8	4.1	2.6	0.63	5.3
	3	21.7	3.7	2.5	0.68	6.3
	4	—	3.1	1.4	0.45	10.8

[0103] It is both twice [more than] the swelling scale factor when absorbing the swelling scale factor when absorbing tap water, and artificial sea water of this, and the water bloating tendency rubber concerning this example has a swelling scale-factor ratio close to 1 so that clearly from Table 1. On the other hand, since the liquid absorption scale factor of a liquid absorption agent is under 5 g/g, both the swelling scale factors of the water bloating tendency rubber for the comparison of the example 1 of a comparison are under 2 double. Moreover, the water bloating tendency rubber for the comparison of the example 2 of a comparison - the example 4 of a comparison has a swelling scale-factor ratio extremely smaller than 1. Furthermore, this consumption of the water bloating tendency rubber for the comparison of the example 2 of a comparison - the example 4 of a comparison is 5mg/l. or more to the consumption of potassium permanganate of the water bloating tendency rubber concerning this example being less than 5 mg/l.

[0104] That is, it turns out that the water bloating tendency rubber concerning this example does not almost have the difference of both the swelling scale factor while it is excellent in the swelling scale factor when absorbing the swelling scale factor when absorbing tap water, and artificial sea water, and the leached moiety (meltable component) is moreover reduced rather than the water bloating tendency rubber for a comparison so that clearly from the result of an example 1 - an example 8, and the example 1 of a comparison - the example 4 of a comparison.

[0105]

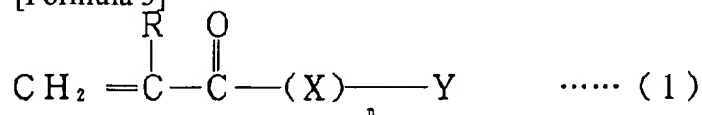
[Effect of the Invention] The water bloating tendency rubber of this invention according to claim 1 is a configuration containing the liquid absorption agent which consists of an alkaline-earth-metal salt of the copolymer led from the monomer component containing an anionic monomer and a nonionic monomer as mentioned above.

[0106] Moreover, the water bloating tendency rubber of this invention according to claim 2 is the configuration that the liquid absorption scale factor of the liquid absorption agent to artificial sea water is more than 5 g/g, as mentioned above. Furthermore, the water bloating tendency rubber of this invention according to claim 3 is a configuration to which the above-mentioned liquid absorption agent comes to carry out copolymerization of the alkaline-earth-metal salt of an anionic monomer, and the nonionic monomer as mentioned above. Moreover, for the water bloating tendency rubber of this

invention according to claim 4, a nonionic monomer is a general formula (1) as mentioned above.

[0107]

[Formula 3]



[0108] (R expresses a hydrogen atom or a methyl group among a formula, and X expresses the oxy-alkylene group of the carbon numbers 2-4 whose mole fractions of the oxyethylene radical to all oxy-alkylene groups are more than 50 mol %.) the oxy-alkylphenyl radical on which Y has 1-3 alkyl groups of carbon numbers 1-9 as the alkoxy group of carbon numbers 1-5, a phenoxy group, or a substituent -- expressing -- n -- an average -- the integer of 3-100 -- expressing -- it is the configuration which is the acrylic ester system monomer expressed (meta). Furthermore, the water bloating tendency rubber of this invention according to claim 5 is the configuration that a nonionic monomer is methoxy polyethylene-glycol methacrylate, as mentioned above. Moreover, the water bloating tendency rubber of this invention according to claim 6 is the configuration that alkaline earth metal is magnesium, as mentioned above.

[0109] The swelling scale factor in the case of a swelling scale factor being high and absorbing the water near Shimizu or Shimizu, such as tap water, by this, There is almost no difference with the swelling scale factor in the case of absorbing aquosity liquids, such as hard water containing salts, polyvalent metal ion, etc., and seawater, cement water. And the leached moiety (meltable component) eluted into water and an aquosity liquid does so the effectiveness that the water bloating tendency rubber reduced conventionally can be offered.

[Translation done.]

* NOTICES *

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2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

TECHNICAL FIELD

[Field of the Invention] This invention relates to the water bloating tendency rubber suitably offered as water cutoff material in a civil work, an construction work, etc.

[Translation done.]

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PRIOR ART

[Description of the Prior Art] The water absorption agent which shows the salt atmosphere which was excellent to aqueous liquids containing polyvalent metal ion etc., such as hard water and seawater, conventionally is known (JP,2-253845,A). This water absorption agent (liquid absorption agent) consists of cross linked polymer which comes to copolymerize the acrylic ester system monomer which has specific structure (meta), and a water-soluble carboxyl group content partial saturation monomer under existence of a cross linking agent. And this water absorption agent is excellent in the liquid absorption scale factor which absorbs the above-mentioned aqueous liquid, and, moreover, is equipped with the property that this liquid absorption scale factor does not fall with time.

[Translation done.]

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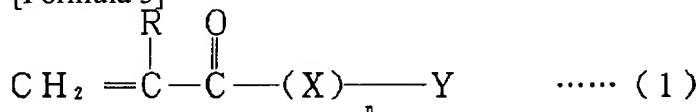
EFFECT OF THE INVENTION

[Effect of the Invention] The water bloating tendency rubber of this invention according to claim 1 is a configuration containing the liquid absorption agent which consists of an alkaline-earth-metal salt of the copolymer led from the monomer component containing an anionic monomer and a nonionic monomer as mentioned above.

[0106] Moreover, the water bloating tendency rubber of this invention according to claim 2 is the configuration that the liquid absorption scale factor of the liquid absorption agent to artificial sea water is more than 5 g/g, as mentioned above. Furthermore, the water bloating tendency rubber of this invention according to claim 3 is a configuration to which the above-mentioned liquid absorption agent comes to carry out copolymerization of the alkaline-earth-metal salt of an anionic monomer, and the nonionic monomer as mentioned above. Moreover, for the water bloating tendency rubber of this invention according to claim 4, a nonionic monomer is a general formula (1) as mentioned above.

[0107]

[Formula 3]



[0108] (R expresses a hydrogen atom or a methyl group among a formula, and X expresses the oxy-alkylene group of the carbon numbers 2-4 whose mole fractions of the oxyethylene radical to all oxy-alkylene groups are more than 50 mol %.) the oxy-alkylphenyl radical on which Y has 1-3 alkyl groups of carbon numbers 1-9 as the alkoxy group of carbon numbers 1-5, a phenoxy group, or a substituent -- expressing -- n -- an average -- the integer of 3-100 -- expressing -- it is the configuration which is the acrylic ester system monomer expressed (meta). Furthermore, the water bloating tendency rubber of this invention according to claim 5 is the configuration that a nonionic monomer is methoxy polyethylene-glycol methacrylate, as mentioned above. Moreover, the water bloating tendency rubber of this invention according to claim 6 is the configuration that alkaline earth metal is magnesium, as mentioned above.

[0109] The swelling scale factor in the case of a swelling scale factor being high and absorbing the water near Shimizu or Shimizu, such as tap water, by this, There is almost no difference with the swelling scale factor in the case of absorbing aqueous liquids, such as hard water containing salts, polyvalent metal ion, etc., and seawater, cement water. And the leached moiety (meltable component) eluted into water and an aqueous liquid does so the effectiveness that the water bloating tendency rubber reduced conventionally can be offered.

[Translation done.]

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] However, if the above-mentioned conventional water absorption agent is mixed with an elastomer and it uses as water bloating tendency rubber, a trouble as shown below will be produced. That is, the water bloating tendency rubber containing the above-mentioned conventional water absorption agent swells greatly, when the water near Shimizu, such as tap water, is contacted, but when the water which contains polyvalent metal ion, such as cement water, so much is contacted, it does not swell a few. That is, since the difference of the swelling scale factor by the class of water which contacts was large, it was what leaves a problem to the water cutoff engine performance and endurance.

[0004] Moreover, since comparatively a lot of leached moieties were eluted when an aquosity liquid is contacted, the water bloating tendency rubber containing the above-mentioned conventional water absorption agent was that by which a problem remains in water cutoff in the application field in which altitude is asked for safety in addition.

[0005] This invention is made in view of the above-mentioned conventional trouble. The purpose The swelling scale factor in the case of absorbing the water near Shimizu or Shimizu, such as tap water, There is almost no difference with the swelling scale factor in the case of absorbing aquosity liquids, such as hard water containing salts, polyvalent metal ion, etc., and seawater, cement water. And the leached moiety eluted into water and an aquosity liquid is to offer water bloating tendency rubber excellent in the water cutoff engine performance reduced conventionally, endurance, and safety.

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MEANS

[Means for Solving the Problem] The water bloating tendency rubber containing the liquid absorption agent which consists of an alkaline-earth-metal salt of the copolymer led from the monomer component containing an anionic monomer and a nonionic monomer as a result of inquiring wholeheartedly that an invention-in-this-application person etc. should attain the above-mentioned purpose The swelling scale factor in the case of absorbing the water near Shimizu or Shimizu, such as tap water, There is almost no difference with the swelling scale factor in the case of absorbing aqueous liquids, such as hard water containing salts, polyvalent metal ion, etc., and seawater, cement water, and it finds out that the leached moiety (meltable component) eluted into water and an aqueous liquid is moreover reduced conventionally, and came to complete this invention.

[0007] That is, the water bloating tendency rubber of invention according to claim 1 is characterized by including the liquid absorption agent which consists of an alkaline-earth-metal salt of the copolymer led from the monomer component containing an anionic monomer and a nonionic monomer, in order to solve the above-mentioned technical problem.

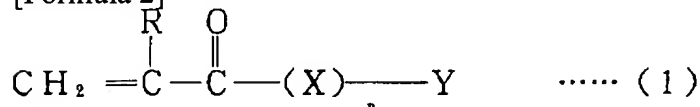
[0008] The water bloating tendency rubber of invention according to claim 2 is characterized by the liquid absorption scale factor of the liquid absorption agent to artificial sea water being more than 5 g/g in water bloating tendency rubber according to claim 1, in order to solve the above-mentioned technical problem.

[0009] In order that the water bloating tendency rubber of invention according to claim 3 may solve the above-mentioned technical problem, in water bloating tendency rubber according to claim 1 or 2, the above-mentioned liquid absorption agent is characterized by coming to carry out copolymerization of the alkaline-earth-metal salt of an anionic monomer, and the nonionic monomer.

[0010] For the water bloating tendency rubber of invention according to claim 4, in order to solve the above-mentioned technical problem, it sets to water bloating tendency rubber given in claim 1 thru/or any 1 term of 3, and a nonionic monomer is a general formula (1).

[0011]

[Formula 2]



[0012] (R expresses a hydrogen atom or a methyl group among a formula, and X expresses the oxy-alkylene group of the carbon numbers 2-4 whose mole fractions of the oxyethylene radical to all oxy-alkylene groups are more than 50 mol %.) Y expresses the alkoxy group of carbon numbers 1-5, a phenoxy group, or the oxy-alkylphenyl radical that has 1-3 alkyl groups of carbon numbers 1-9 as a substituent. n -- an average -- the integer of 3-100 -- expressing -- it is characterized by being the acrylic ester system monomer expressed (meta).

[0013] The water bloating tendency rubber of invention according to claim 5 is characterized by a nonionic monomer being methoxy polyethylene-glycol methacrylate in water bloating tendency rubber

given in claim 1 thru/or any 1 term of 4, in order to solve the above-mentioned technical problem.

[0014] The water bloating tendency rubber of invention according to claim 6 is characterized by alkaline earth metal being magnesium in water bloating tendency rubber given in claim 1 thru/or any 1 term of 5, in order to solve the above-mentioned technical problem.

[0015] According to the above-mentioned configuration, the liquid absorption agent contained in water bloating tendency rubber is the alkaline-earth-metal salt of the copolymer led from the monomer component containing an anionic monomer and a nonionic monomer. Thereby, a swelling scale factor is high, there is almost no difference with the swelling scale factor in the case of absorbing aqueous liquids, such as hard water containing the swelling scale factor in the case of absorbing the water near Shimizu or Shimizu, such as tap water, salts, polyvalent metal ion, etc., and seawater, cement water, and, moreover, the water bloating tendency rubber with which the leached moiety (meltable component) eluted into water and an aqueous liquid was reduced conventionally can be offered.

[0016] This invention is explained in detail below. Artificial sea water in this invention shows the water solution with which it dissolves and it becomes deionized water as the concentration in artificial sea water which should prepare a calcium sulfate (CaSO_4), magnesium sulfate (MgSO_4), a magnesium chloride (MgCl_2), potassium chloride (KCl), and a sodium chloride (NaCl) serves as CaSO_4 3.32 g/kg, KCl :0.72 g/kg, and NaCl :26.69 g/kg. : 1.38 g/kg, MgSO_4 : 2.10 g/kg, MgCl_2 :

[0017] The water bloating tendency rubber concerning this invention contains the liquid absorption agent and the elastomer. The above-mentioned liquid absorption agent is the alkaline-earth-metal salt of the copolymer led from the monomer component containing an anionic monomer and a nonionic monomer. The above-mentioned alkaline earth metal has magnesium and more desirable calcium, and especially its magnesium is desirable. In addition, the above-mentioned monomer component may contain other monomers other than an anionic monomer and a nonionic monomer.

[0018] The above-mentioned anionic monomer is not especially limited like the after-mentioned that what is necessary is just the monomer which can form alkaline earth metal and a salt. As an anionic monomer, specifically For example, an acrylic acid (meta), Partial saturation monocarboxylic acid system monomers, such as a crotonic acid; A maleic acid, a fumaric acid, Partial saturation dicarboxylic acid system monomers, such as an itaconic acid and a citraconic acid; A vinyl sulfonic acid, An allyl compound sulfonic acid, a metallyl sulfonic acid, a styrene sulfonic acid, 2-acrylamide - isobutane sulfonic acid, Sulfoethyl (meta) acrylate, sulfopropyl (meta) acrylate, Partial saturation sulfonic-acid system monomers, such as 2-hydroxy sulfopropyl (meta) acrylate; (meta) acrylamide methane phosphonic acid, 2-(meta) acrylamide Partial saturation phosphonic acid system monomers, such as - isobutane phosphonic acid, etc. are mentioned. These anionic monomer may be used independently, and may mix two or more kinds suitably, and may be used. A partial saturation monocarboxylic acid system monomer is more desirable among the monomers of the above-mentioned instantiation, an acrylic acid (meta) is still more desirable, and especially a methacrylic acid is desirable.

[0019] The above-mentioned nonionic monomer is not limited especially that what is necessary is just as copolymerizable a monomer as an anionic monomer. The acrylic ester system monomer; 2-hydroxyethyl (meta) acrylate specifically expressed with said general formula (1) as a nonionic monomer (meta), Polyethylene-glycol monochrome (meta) acrylate, polypropylene-glycol monochrome (meta) acrylate, Hydroxyl-group content partial saturation monomers, such as allyl alcohol and vinyl alcohol; (meta) Acrylamide, Amide system partial saturation monomers, such as N-vinyl acetamide and t-butyl (meta) acrylamide; (meta) Acrylic ester, Nitril system partial saturation monomers [, such as hydrophobic partial saturation monomer; (meta) acrylonitrile], such as styrene, 2-methyl styrene, and vinyl acetate; Ethylene, A propylene, 1-butene, an isobutylene, alpha-amylene, 2-methyl -1-butene, 3-methyl Alpha olefin system monomers, such as -1-butene (alpha-iso amylene), 1-hexene, and 1-heptene; alkoxy polyalkylene glycol monochrome (meta) acrylate etc. is mentioned. moreover, as the above-mentioned acrylic ester (meta) system monomer Specifically For example, methoxy polyethylene-glycol monochrome (meta) acrylate, Butoxy polyethylene-glycol monochrome (meta) acrylate, methoxy polyethylene-glycol polypropylene-glycol monochrome (meta) acrylate, Methoxy polyethylene-glycol polybutylene glycol monochrome (meta) acrylate, Ethoxy polyethylene-glycol polypropylene-glycol

monochrome (meta) acrylate, ethoxy polyethylene-glycol polybutylene glycol monochrome (meta) acrylate, etc. are mentioned. These nonionic monomer may be used independently, and may mix two or more kinds suitably, and may be used. The acrylic ester system monomer expressed with said general formula (1) among the monomers of the above-mentioned instantiation (meta) is more desirable, and especially methoxy polyethylene-glycol methacrylate is desirable. Moreover, when using methoxy polyethylene-glycol methacrylate as a nonionic monomer, the number of average addition mols of ethyleneoxide has desirable within the limits of five mols - 50 mols. That is, when Y is a methoxy group, within the limits of n of 5-50 is desirable [X in a general formula (1) is an oxyethylene radical, and R is a methyl group, and].

[0020] Although especially the rate of the anionic monomer in the above-mentioned the ratio of an anionic monomer and a nonionic monomer, i.e., copolymer component, is not limited, 5 % of the weight - 95% of the weight of its within the limits is more desirable, and 10 % of the weight - 70% of the weight of its within the limits is still more desirable. When there are few rates of an anionic monomer than 5 % of the weight, there is an inclination for the leached moiety in the copolymer obtained to increase. Moreover, when there are more rates of an anionic monomer than 95 % of the weight, the liquid absorption scale factor of a liquid absorption agent becomes low. Therefore, there is a possibility that water bloating tendency rubber equipped with the physical properties for which it asks may not be obtained.

[0021] The approach, i.e., the manufacture approach of a liquid absorption agent, of manufacturing the alkaline-earth-metal salt of the copolymer led from the monomer component containing an anionic monomer and a nonionic monomer After making for example, not the thing limited especially but ** anionic monomer, and chlorides, such as a calcium chloride and a magnesium chloride, react and forming the alkaline-earth-metal salt of an anionic monomer, The approach and ** anionic monomer to which copolymerization of the nonionic monomer is added and carried out, The approach and ** anionic monomer to which copolymerization of the nonionic monomer is added and carried out after making hydroxides, such as a calcium hydroxide and a magnesium hydroxide, react and forming the alkaline-earth-metal salt of an anionic monomer, After making carbonates, such as a calcium carbonate and a magnesium carbonate, react and forming the alkaline-earth-metal salt of an anionic monomer, After carrying out copolymerization of the approach and ** anionic monomer to which copolymerization of the nonionic monomer is added and carried out, and the nonionic monomer, After carrying out copolymerization of the approach and ** anionic monomer which add the above-mentioned chloride and form an alkaline-earth-metal salt, and the nonionic monomer, After carrying out copolymerization of the approach and ** anionic monomer which add the above-mentioned hydroxide and form an alkaline-earth-metal salt, and the nonionic monomer, various approaches, such as the approach of adding the above-mentioned carbonate and forming an alkaline-earth-metal salt, are employable. Moreover, after mixing an anionic monomer, a nonionic monomer, and a chloride, an above-mentioned hydroxide or an above-mentioned carbonate, copolymerization can be carried out and a liquid absorption agent can also be manufactured. The approach of ** and the approach of ** are more desirable among these approaches, and especially the approach of ** is desirable. Moreover, when adopting the approach of the above-mentioned **, especially a hydroxide has a desirable magnesium hydroxide. Since the solubility to water is large, the magnesium salt of an anionic monomer is suitable for a polymerization reaction.

[0022] Although the alkaline-earth-metal salt of the copolymer in the invention in this application is not clear about the reason whose leached moiety decreases compared with alkali-metal salts, such as sodium salt and potassium salt, it guesses as follows.

[0023] That is, it is guessed that it is for the solubility of a fusibility polymer to fall as a result of constructing a bridge over this fusibility polymer two-dimensional or in three dimensions with alkaline earth metal although a leached moiety uses a fusibility polymer as a principal component.

[0024] Well-known various approaches, for example, a solution polymerization method, a suspension-polymerization method, an opposition suspension-polymerization method, etc. can be conventionally used for a polymerization method. In addition, although especially the stirring approach at the time of performing a polymerization reaction is not limited, it is more desirable to stir subdividing the gel

copolymer (it mentioning later) to generate according to this double arm mold kneader's shearing force using a double arm mold kneader as stirring equipment.

[0025] Although it is not limited, since low-temperature one becomes large, its molecular weight of a copolymer is comparatively desirable, and since a polymerization reaction completes especially reaction temperature, within the limits of 20 degrees C - 100 degree C is still more desirable [reaction temperature]. In addition, what is necessary is just to set up reaction time suitably according to the class (property) of reaction temperature, a monomer component, a polymerization initiator, a solvent, etc., etc., combination, the amount used, etc. so that the above-mentioned polymerization reaction may be completed.

[0026] A polymerization initiator can be used in case copolymerization of the monomer component is carried out. Specifically as this polymerization initiator, they are peroxides, such as a hydrogen peroxide, benzoyl peroxide, and cumene hydroperoxide.; Azo compounds, such as a 2 and 2'-azobisisobutyronitril, 2, 2'-azobis (2-amidinopropane) hydrochloride; radical generating agents (radical polymerization initiator), such as persulfate, such as ammonium persulfate, sodium persulfate, and potassium persulfate, etc. are mentioned. These polymerization initiators may be used independently, and may mix two or more kinds suitably, and may be used. Furthermore, the redox system initiator which comes to combine these radical generating agent and reducing agents, such as a sodium hydrogensulfite, and L-ascorbic acid (salt), ferrous salt, may be used. In addition, instead of using a polymerization initiator, a radiation, an electron ray, ultraviolet rays, etc. may be irradiated, and a polymerization initiator and the exposure of these radiations, an electron ray, ultraviolet rays, etc., etc. may be used together.

[0027] Although especially the amount of the polymerization initiator used is not limited, 0.001 % of the weight - 10% of the weight of its within the limits is more desirable to a monomer component, and 0.01 % of the weight - 1% of the weight of its within the limits is still more desirable. Moreover, although especially the amount of the reducing agent used in the case of using a redox system initiator is not limited, its within the limits of 0.01-5 is more desirable to a radical generating agent at a weight ratio, and its within the limits of 0.05-2 is still more desirable.

[0028] Moreover, in case copolymerization of the monomer component is carried out, a cross linking agent may be used if needed. As this cross linking agent, specifically For example, a divinylbenzene, ethylene GURIKORUJI (meta) acrylate, Diethylene GURIKORUJI (meta) acrylate, TORIECHIRENGURIKORUJI (meta) acrylate, Propylene GURIKORUJI (meta) acrylate, polyethylene GURIKORUJI (meta) acrylate, TORIMECHI roll pro pantry (meta) acrylate, pen TAERISURITORUJI (meta) acrylate, Pen TAERISURITORUTORI (meta) acrylate, N, and N-methylenebis acrylamide, An isocyanuric acid triaryl, trimethylol propane diaryl ether, etc., The compound which has two or more ethylene system partial saturation radicals in 1 molecule; Ethylene glycol, A diethylene glycol, triethylene glycol, a polyethylene glycol, A glycerol, polyglycerin, propylene glycol, a polypropylene glycol, Polyvinyl alcohol, pentaerythritol, diethanolamine, Triethanolamine, sorbitol, sorbitan, a glucose, mannite, Polyhydric alcohol, such as Manni Tan, cane sugar, and grape sugar; Ethylene glycol diglycidyl ether, Polyethylene glycol diglycidyl ether, glycerol diglycidyl ether, Propylene glycol diglycidyl ether, polypropylene glycol diglycidyl ether, Neopentyl glycol diglycidyl ether, 1, 6-hexanediol diglycidyl ether, The Pori epoxy compounds, such as trimethylol propane diglycidyl ether, trimethylolpropane triglycidyl ether, and glycerol triglycidyl ether, etc. are mentioned. These cross linking agents may be used independently, and they may be mixed suitably and two or more kinds may be used for them.

[0029] By using a cross linking agent, the crosslinking density of a copolymer is controllable. What is necessary is not to limit especially the amount of the cross linking agent used, and just to set it up suitably by the class of the monomer component used or cross linking agent, the crosslinking density for which it asks. specifically, about 0.0005 to 0.02 within the limits has [the amount of the cross linking agent used] a more desirable mole ratio to a monomer component -- within the limits of 0.001-0.01 is still more desirable. In addition, when using polyhydric alcohol as a cross linking agent, they are after a polymerization reaction and a copolymer. It is desirable to heat-treat at 150 degrees C - 250 degree C.

Moreover, when using the Pori epoxy compound as a cross linking agent, it is desirable after a polymerization reaction to heat-treat a copolymer at 50 degrees C - 250 degree C.

[0030] Furthermore, in case copolymerization of the monomer component is carried out, a solvent may be used if needed. Specifically as this solvent, aqueous solvents, such as water; cyclohexane, a toluene; methanol, ethanol, an acetone, dimethylformamide, and dimethyl sulfoxide, etc. are mentioned. These solvents may be used independently, and may mix two or more kinds suitably, and may be used. Among the solvents of the above-mentioned instantiation, since safety can manufacture a liquid absorption agent still more highly and cheaply, the mixture of water and water, and an aqueous solvent has it. [more desirable] In addition, although especially the concentration of the monomer component in the case of using a solvent is not limited, 20 % of the weight - 80% of the weight of its within the limits is more desirable, and 30 % of the weight - 60% of the weight of its within the limits is still more desirable. While a polymerization reaction is easily controllable by making concentration of the monomer component in the solution containing this monomer component, a polymerization initiator, a cross linking agent, etc. into within the limits of the above, the yield of a copolymer can be raised and this copolymer can be obtained economically.

[0031] After a polymerization reaction, since it is obtained by gel, the alkaline-earth-metal salt of a copolymer dries the alkaline-earth-metal salt of this gel copolymer, after performing predetermined actuation of washing, a crack, etc. remaining as it is or if needed. Although especially drying temperature is not limited, within the limits of 50 degrees C - 180 degree C being suitable and its within the limits which is 100 degree C to 170 degree C are the optimal. Moreover, after a dry matter operates grinding etc. and carries out grain refining, it performs classification actuation of sieving etc. if needed. Thereby, the liquid absorption agent more than 5 g/g is obtained for the liquid absorption scale factor to artificial sea water.

[0032] Moreover, in order to reduce a leached moiety and to raise the safety of this liquid absorption agent further by decreasing the unreacted monomer component which remains to a liquid absorption agent, it is desirable to use a reducing agent and to process the alkaline-earth-metal salt of a gel copolymer or its dry matter. Specifically as this reducing agent, a sodium sulfite, potassium sulfite, ammonium sulfite, a sodium hydrogensulfite, a potassium hydrogensulfite, hydrogen sulfite ammonium, a sodium thiosulfate, potassium thiosulfate, ammonium thiosulfate, L-ascorbic acid, ammonia, monoethanolamine, a glucose, etc. are mentioned. These reducing agents may be used independently, and may mix two or more kinds suitably, and may be used. A sodium sulfite, a sodium hydrogensulfite, and a sodium thiosulfate are more desirable among the reducing agents of the above-mentioned instantiation. although especially the amount of the reducing agent used is not limited, specifically, about 0.0001 to 0.02 within the limits has a more desirable mole ratio to the used monomer component - within the limits of 0.001-0.01 is still more desirable.

[0033] Although especially the configuration of a liquid absorption agent etc. is not limited, it is desirable that the mean particle diameter is 5 micrometers - about 70 micrometers, and it is more desirable that it is 10 micrometers - about 50 micrometers so that it can mix with an elastomer to homogeneity (distribution) and water bloating tendency rubber can swell in homogeneity. In addition, the above-mentioned mean particle diameter is volume mean particle diameter.

[0034] Especially the above-mentioned elastomer is not limited and well-known various compounds can be conventionally used for it. Specifically as this elastomer, they are polybutadiene rubber, polyisoprene rubber, styrene-butadiene copolymer rubber, chloroprene rubber, isoprene-isobutylene copolymer rubber, and ethylene. - It is alpha. - Ethylene, such as olefine copolymer rubber and ethylene propylene rubber (EPDM) rubber - alpha - Synthetic rubber, such as olefin-nonconjugated diene copolymer rubber; the synthetic-resin; natural rubber which has rubber elasticity, such as chlorinated polyethylene, chlorosulfonated polyethylene, an ethylene-vinylacetate copolymer, plasticized polyvinyl chloride, and polyurethane, is mentioned. These elastomers may be used independently, and may mix two or more kinds suitably, and may be used.

[0035] The rate of the liquid absorption agent and elastomer in water bloating tendency rubber, i.e., the weight ratio of a liquid absorption agent and an elastomer, has desirable within the limits of 5:95-50:50,

and its within the limits of 15:85-40:60 is more desirable. When there are few weight ratios of a liquid absorption agent than the above-mentioned range (less than 5), since water bloating tendency rubber cannot fully swell, it is not desirable. Moreover, when there are more weight ratios of a liquid absorption agent than the above-mentioned range (50 is exceeded), since water bloating tendency rubber becomes weak and reinforcement falls, it is not desirable.

[0036] Although the especially manufacture approach of water bloating tendency rubber, i.e., the mixed (kneading) approach of a liquid absorption agent and an elastomer, is not limited, it is desirable to mix to homogeneity using the well-known mechanical technique with which manufacture of rubber goods of kneading using kneading machines, such as a roll mill and a Banbury mixer, etc. is presented conventionally. Moreover, what is necessary is just to fabricate this mixture in a predetermined configuration using the shaping approaches, such as extrusion molding and press forming, if needed. Thereby, water bloating tendency rubber is obtained.

[0037] As for water bloating tendency rubber, the additive other than a liquid absorption agent and an elastomer may be added if needed. As this additive, a vulcanizing agent, a vulcanization accelerator, a vulcanization assistant, an inorganic bulking agent, a reinforcing agent, a softener, a plasticizer, a coloring agent, an ultraviolet ray absorbent, lubricant, an antioxidant, etc. are mentioned, for example. These additives may be used independently, and may mix two or more kinds suitably, and may be used. the amount of the additive used -- the total quantity of a liquid absorption agent and an elastomer -- receiving -- for example, 100 or less % of the weight -- desirable -- Although it is good, it is not limited especially that what is necessary is just 0.1 % of the weight - 60% of the weight of within the limits, then the amount which does not spoil the physical properties (for example, reinforcement etc.) of water bloating tendency rubber. Moreover, especially the addition approach of an additive is not limited.

[0038] As the above-mentioned vulcanizing agent, although sulfur, flower of sulfur, deoxidation sulfur, precipitated sulfur, colloid sulfur, a sulfur chloride; zinc oxide, a magnesium oxide, a selenium, tellurium; peroxide; nitroaromatic, etc. are mentioned, specifically, it is not limited especially. These vulcanizing agents may be used independently, and may mix two or more kinds suitably, and may be used. As opposed to the total quantity of a liquid absorption agent and an elastomer, the amount of the vulcanizing agent used is not 0.1 % of the weight - 10% of the weight of within the limits, then the thing limited especially, although it is good.

[0039] As the above-mentioned vulcanization accelerator, although guanidine, aldehyde ammonia, aldehyde amines, a nitroso compound, thiazoles, thiazoline, imidazoline, thiourea, thio-acid salts, the Calvi thio-acid salts, iso thiourea salts, etc. are mentioned, specifically, it is not limited especially. These vulcanization accelerators may be used independently, and may mix two or more kinds suitably, and may be used. As opposed to the total quantity of a liquid absorption agent and an elastomer, the amount of the vulcanization accelerator used is not 0.1 % of the weight - 10% of the weight of within the limits, then the thing limited especially, although it is good.

[0040] As the above-mentioned vulcanization assistant, although a sodium hydroxide, a calcium oxide, a magnesium oxide (magnesia), a zinc white, lead(II) oxide, etc. are mentioned, specifically, it is not limited especially. These vulcanization assistant may be used independently, and may mix two or more kinds suitably, and may be used. As opposed to the total quantity of a liquid absorption agent and an elastomer, the amount of the vulcanization assistant used is not 0.1 % of the weight - 10% of the weight of within the limits, then the thing limited especially, although it is good.

[0041] Although what is necessary is just to heat-treat for [for / 1 minute / -] 30 minutes at 100 degree C to 200 degree C in case an elastomer is vulcanized, especially processing conditions are not limited. In addition, what is necessary is just to perform this heat-treatment after the time of shaping of the mixture which consists of a liquid absorption agent, an elastomer, etc., or shaping.

[0042] Moreover, as the above-mentioned inorganic bulking agent, although inorganic substances, such as a titanium dioxide, a calcium carbonate, a zinc white, clay, a kaolin, a bentonite, a silica, talc, a zeolite, and white carbon, are mentioned, specifically, it is not limited especially. These inorganic bulking agents may be used independently, and may mix two or more kinds suitably, and may be used. As opposed to the total quantity of a liquid absorption agent and an elastomer, the amount of the

inorganic bulking agent used is not 10 % of the weight - 50% of the weight of within the limits, then the thing limited especially, although it is good.

[0043] The water bloating tendency rubber concerning this invention is a configuration containing the liquid absorption agent which consists of an alkaline-earth-metal salt of the copolymer led from the monomer component containing an anionic monomer and a nonionic monomer as mentioned above.

[0044] Moreover, water bloating tendency rubber is the configuration that the liquid absorption scale factor of the liquid absorption agent to artificial sea water is more than 5 g/g, as mentioned above.

Furthermore, water bloating tendency rubber is a configuration to which the above-mentioned liquid absorption agent comes to carry out copolymerization of the alkaline-earth-metal salt of an anionic monomer, and the nonionic monomer as mentioned above. Moreover, water bloating tendency rubber is the configuration that a nonionic monomer is an acrylic ester system monomer expressed with said general formula (1) (meta), as mentioned above. Furthermore, water bloating tendency rubber is the configuration that a nonionic monomer is methoxy polyethylene-glycol methacrylate, as mentioned above. Moreover, water bloating tendency rubber is the configuration that alkaline earth metal is magnesium, as mentioned above.

[0045] Thereby, a swelling scale factor is high, there is almost no difference with the swelling scale factor in the case of absorbing aquosity liquids, such as hard water containing the swelling scale factor in the case of absorbing the water near Shimizu or Shimizu, such as tap water, salts, polyvalent metal ion, etc., and seawater, cement water, and, moreover, the water bloating tendency rubber with which the leached moiety (meltable component) eluted into water and an aquosity liquid was reduced conventionally can be offered. Water bloating tendency rubber is suitably offered as the water cutoff material in civil works, construction works, etc., such as tunnel excavation, the water cutoff material of tap water, the exsorption prevention material which prevents the exsorption to the exterior of industrial waste water, etc. In addition, water bloating tendency rubber may be fabricated by predetermined configurations, such as a letter of a block.

[Translation done.]

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EXAMPLE

[Example] Hereafter, although an example and the example of a comparison explain this invention to a detail further, this invention is not limited at all by these. In addition, the engine performance of a liquid absorption agent and water bloating tendency rubber was measured by the following approaches. Moreover, the "section" given in an example and the example of a comparison shows the "weight section."

[0047] (a) About 1g of liquid absorption scale-factor liquid absorption agents of a liquid absorption agent was put into the tea bag type bag at homogeneity, and it was immersed all over artificial sea water. Weight W1 of a tea bag type bag after pulling up a tea bag type bag after 24-hour standing and performing a fixed time amount ridge (g) It measured. Moreover, same actuation is performed without using a liquid absorption agent, and it is the weight W0 of the tea bag type bag at that time (g). It measured. these weight W1 and W0 from -- weight of a degree type, and a liquid absorption scale-factor (g/g) = (weight W1 (g)-weight W0 (g)) / liquid absorption agent (g) -- following -- liquid absorption scale factor (g/g) It computed. [and] In addition, this liquid absorption scale factor is a balanced value.

[0048] (b) Cut off the bloating tendency water bloating tendency rubber of water bloating tendency rubber so that it may become 3mm in thickness on a 2cmx2cm square, and create a test piece, and it is the weight. (g) After measuring, this test piece was immersed all over tap water or artificial sea water. The weight after pulling up a test piece after standing for 30 days and wiping off moisture lightly through a filter paper (g) It measured. And the degree type from these weight and weight of the test piece after swelling scale-factor (twice) = immersion (g) The swelling scale factor (twice) was computed according to the weight (g) of the test piece before /immersion.

[0049] Moreover, it asked for the ratio (swelling scale factor when absorbing the swelling scale factor / tap water when absorbing artificial sea water) of the swelling scale factor when absorbing tap water, and the swelling scale factor when absorbing artificial sea water, and this value was made into the swelling scale-factor ratio.

[0050] (c) Elution nature JIS of water bloating tendency rubber K Based on the dissolution test judging approach of 6353 "the rubber for waterworks", the elution nature of water bloating tendency rubber was measured. First, it is water bloating tendency rubber the thickness of 3mm, and the surface area of 20cm² It cut off and the test piece was created so that it might become, and this test piece was immersed into deionized water 1L. This deionized water was extracted after 24-hour standing, and this was made into sample water. Moreover, same actuation was performed without immersing a test piece, and blank sample water was prepared. On the other hand, they are N / 100 potassium permanganate water solutions. N / 100 sodium-oxalate water solutions are prepared, and it is **. N / 100 sodium-oxalate water solutions are used. N / 100 potassium permanganate water solutions are titrated, and it is **. The factor of N / 100 potassium permanganate water solutions was computed.

[0051] subsequently -- this -- Above-mentioned sample water and blank sample water were titrated using N / 100 potassium permanganate water solutions. And according to the degree type, the consumption (mg/l) of potassium permanganate was computed and this value estimated the elution nature of water bloating tendency rubber.

[0052] $A = (a - b) - f \times (1000 / I) \times B$ -- however A : Consumption a of potassium permanganate (mg/l) : It required for sample water. Total quantity b of N / 100 potassium permanganate water solutions (ml) : It required for blank sample water. The total quantity (ml) f of N / 100 potassium permanganate water solutions : Factor I of N / 100 potassium permanganate water solutions : Amount B of sample water (ml) : It is 0.316 (mg/l).

[0053] [Example 1] Content volume equipped with a thermometer, nitrogen gas installation tubing, and an agitator To the 600ml reactor made from plastics, it is a 35-% of the weight methacrylic-acid magnesium water solution as an alkaline-earth-metal salt of an anionic monomer. The 203 sections, methoxy polyethylene-glycol methacrylate as a nonionic monomer The 169 sections, the ion-exchange-water 23.2 section as a solvent, and the polyethylene-glycol diacrylate 0.41 section as a cross linking agent were taught, and it considered as reaction mixture. The number of average addition mols of the ethyleneoxide in the above-mentioned methoxy polyethylene-glycol methacrylate is nine mols. Moreover, the number of average addition mols of the ethyleneoxide in polyethylene-glycol diacrylate is eight mols.

[0054] That is, both were taught so that the concentration of the sum total of the above-mentioned methacrylic-acid component and methoxy polyethylene-glycol methacrylate in reaction mixture, i.e., the concentration of a monomer component, might become 60 % of the weight, while making it the mole ratio of the methacrylic-acid component in a methacrylic-acid magnesium water solution and methoxy polyethylene-glycol methacrylate set to 67:33. Moreover, polyethylene-glycol diacrylate was taught so that the rate to the above-mentioned monomer component might become 0.12-mol %.

[0055] Next, while blowing nitrogen gas into the above-mentioned reaction mixture and driving out dissolved oxygen, nitrogen inert gas replacement of the system of reaction was carried out. Then, 10 % of the weight as a polymerization initiator after carrying out the temperature up of the temperature of reaction mixture to 40 degrees C using a water bath The 2 and 2'-azobis (2-amidinopropane) hydrochloride (Wako Pure Chem Industries make; trade name V-50) water-solution 4.44 section was added. And stirring was stopped after stirring and mixing this reaction mixture. Then, the polymerization reaction was started immediately. The 2 and 2'-azobis (2-amidinopropane) hydrochloride was added so that the rate to a monomer component might become 0.15-mol %.

[0056] In the above-mentioned polymerization reaction, 38 minutes after starting the reaction, the temperature of reaction mixture became 93 degrees C, and reached the peak. In the meantime, the temperature up of the temperature of a water bath was suitably carried out so that it might become almost equal to the temperature of reaction mixture. After the temperature of reaction mixture reached the peak, the temperature of a water bath was maintained at 80 degrees C, and this reaction mixture was riped for 30 minutes. The obtained water gel polymer was taken out after reaction termination, and it cracked in the shape of a particle.

[0057] After drying the cracked water gel polymer at the bottom of a nitrogen air current, and 150 degree C for 1 hour using a hot blast circulation type dryer, the liquid absorption agent of the magnitude of 60 meshes - 100 meshes was obtained by grinding a dry matter using a table-top-type grinder, and classifying at a wire gauze etc. further.

[0058] The liquid absorption scale factor of the obtained liquid absorption agent was measured by the above-mentioned approach. Consequently, the liquid absorption scale factor was 20.8 g/g. It ground further and liquid absorption agent powder was obtained so that mean particle diameter might be set to 15 micrometers using a jet mill in this liquid absorption agent.

[0059] Next, chloroprene rubber as an elastomer In the 100 sections, the magnesium-oxide 4 section as the liquid absorption agent powder 50 section, an above-mentioned vulcanizing agent, and an above-mentioned vulcanization assistant, the zinc-oxide 5 section as a vulcanizing agent, the vulcanization-accelerator 1 section, the lubricant 1 section, the antioxidant 2 section, the calcium-carbonate 20 section as an inorganic bulking agent, and the softener 15 section were mixed. And thickness after kneading this mixture for 20 minutes using a 10 inch trial mill The compound was obtained by extending to 3.5mm. Subsequently, an electric heat press machine is used for the above-mentioned compound. By vulcanizing for 10 minutes at 170 degrees C, the water bloating tendency rubber of the shape of a sheet

with a thickness of 3mm was obtained.

[0060] The bloating tendency and elution nature of water bloating tendency rubber which were obtained were measured by the above-mentioned approach. Consequently, swelling scale factor when absorbing tap water Swelling scale factor when being 3.2 times and absorbing artificial sea water It was 3.0 times and the swelling scale-factor ratio was 0.94. Moreover, consumption of potassium permanganate It was 1.6 mg/l. These results were indicated to Table 1.

[0061] [Example 2] Methoxy polyethylene-glycol methacrylate in an example 1 whose number of average addition mols of ethyleneoxide is nine mols Methoxy polyethylene-glycol methacrylate whose number of average addition mols of ethyleneoxide it replaces with the 169 sections and is 50 mols (nonionic monomer) Except having used the 169 sections, the same reaction and actuation as an example 1 were performed, and the liquid absorption agent was obtained. The liquid absorption scale factor of the obtained liquid absorption agent was 23.3 g/g. This liquid absorption agent was further ground like the example 1, and the liquid absorption agent powder whose mean particle diameter is 32 micrometers was obtained.

[0062] Next, the same actuation as an example 1 was performed using the above-mentioned liquid absorption agent powder, and water bloating tendency rubber was obtained. The bloating tendency and elution nature of water bloating tendency rubber which were obtained were measured. The result was indicated to Table 1.

[0063] [Example 3] Methoxy polyethylene-glycol methacrylate in an example 1 Butoxy polyethylene-glycol methacrylate whose number of average addition mols of ethyleneoxide it replaces with the 169 sections and is 80 mols (nonionic monomer) Except having used the 169 sections, the same reaction and actuation as an example 1 were performed, and the liquid absorption agent was obtained. The liquid absorption scale factor of the obtained liquid absorption agent was 18.3 g/g. This liquid absorption agent was further ground like the example 1, and the liquid absorption agent powder whose mean particle diameter is 74 micrometers was obtained.

[0064] Next, the same actuation as an example 1 was performed using the above-mentioned liquid absorption agent powder, and water bloating tendency rubber was obtained. The bloating tendency and elution nature of water bloating tendency rubber which were obtained were measured. The result was indicated to Table 1.

[0065] [Example 4] It is from the 0.41 sections about the amount of the polyethylene-glycol diacrylate used in an example 1. It changed into the 4.1 sections. That is, the rate to a monomer component polyethylene-glycol diacrylate Except having taught so that it might become 1.5-mol %, the same reaction and actuation as an example 1 were performed, and the liquid absorption agent was obtained. Liquid absorption scale factor of the obtained liquid absorption agent It was 5.5 g/g. This liquid absorption agent was further ground like the example 1, and the liquid absorption agent powder whose mean particle diameter is 7 micrometers was obtained.

[0066] Next, the same actuation as an example 1 was performed using the above-mentioned liquid absorption agent powder, and water bloating tendency rubber was obtained. The bloating tendency and elution nature of water bloating tendency rubber which were obtained were measured. The result was indicated to Table 1.

[0067] [Example 5] To the same reactor as an example 1, it is a 10-% of the weight methacrylic-acid calcium water solution as an alkaline-earth-metal salt of an anionic monomer. The 313 sections, the methoxy polyethylene-glycol methacrylate 68.7 section, the ion-exchange-water 16.9 section, and the polyethylene-glycol diacrylate 0.17 section were taught, and it considered as reaction mixture. The number of average addition mols of the ethyleneoxide in the above-mentioned methoxy polyethylene-glycol methacrylate is nine mols. Moreover, the number of average addition mols of the ethyleneoxide in polyethylene-glycol diacrylate is eight mols.

[0068] That is, both were taught so that the concentration of the methacrylic-acid component in a methacrylic-acid calcium water solution and the monomer component in reaction mixture while making it a mole ratio with methoxy polyethylene-glycol methacrylate set to 67:33 might become 25 % of the weight. Moreover, polyethylene-glycol diacrylate was taught so that the rate to the above-mentioned

monomer component might become 0.12-mol %.

[0069] Next, while blowing nitrogen gas into the above-mentioned reaction mixture and driving out dissolved oxygen, nitrogen inert gas replacement of the system of reaction was carried out. Then, 10 % of the weight after carrying out the temperature up of the temperature of reaction mixture to 50 degrees C using a water bath The 2 and 2'-azobis (2-amidinopropane) hydrochloride water-solution 1.21 section was added. And stirring was stopped after stirring and mixing this reaction mixture. Then, the polymerization reaction was started immediately. The 2 and 2'-azobis (2-amidinopropane) hydrochloride was added so that the rate to a monomer component might become 0.15-mol %.

[0070] In the above-mentioned polymerization reaction, 60 minutes after starting the reaction, the temperature of reaction mixture became 58 degrees C, and reached the peak. In the meantime, the temperature up of the temperature of a water bath was suitably carried out so that it might become almost equal to the temperature of reaction mixture. After the temperature of reaction mixture reached the peak, the temperature of a water bath was maintained at 80 degrees C, and this reaction mixture was riped for 60 minutes. The obtained water gel polymer was taken out after reaction termination, and it cracked in the shape of a particle.

[0071] When desiccation, grinding, etc. made the cracked water gel polymer be the same as that of an example 1, the liquid absorption agent of the magnitude of 60 meshes - 100 meshes was obtained. The liquid absorption scale factor of the obtained liquid absorption agent was 51.3 g/g. This liquid absorption agent was further ground like the example 1, and the liquid absorption agent powder whose mean particle diameter is 23 micrometers was obtained.

[0072] Next, the same actuation as an example 1 was performed using the above-mentioned liquid absorption agent powder, and water bloating tendency rubber was obtained. The bloating tendency and elution nature of water bloating tendency rubber which were obtained were measured. The result was indicated to Table 1.

[0073] [Example 6] The amount of the polyethylene-glycol diacrylate used in an example 5 was changed into the 0.51 sections from the 0.17 sections. That is, except having taught polyethylene-glycol diacrylate so that the rate to a monomer component might become 0.36-mol %, the same reaction and actuation as an example 5 were performed, and the liquid absorption agent was obtained. The liquid absorption scale factor of the obtained liquid absorption agent was 22.4 g/g. This liquid absorption agent was further ground like the example 1, and the liquid absorption agent powder whose mean particle diameter is 18 micrometers was obtained.

[0074] Next, the same actuation as an example 1 was performed using the above-mentioned liquid absorption agent powder, and water bloating tendency rubber was obtained. The bloating tendency and elution nature of water bloating tendency rubber which were obtained were measured. The result was indicated to Table 1.

[0075] [Example 7] To the same reactor as an example 1, it is a 40-% of the weight acrylic-acid magnesium water solution as an alkaline-earth-metal salt of an anionic monomer. The 100.2 sections, 40-% of the weight acrylamide water solution as a nonionic monomer As the 199.8 sections, the ion-exchange-water 73.8 section, and a cross linking agent The 1.5-% of the weight N and N-methylenebis acrylamide water-solution 16.5 section was taught, and it considered as reaction mixture.

[0076] That is, both were taught so that the concentration of the acrylic-acid component in an acrylic-acid magnesium water solution and the monomer component in reaction mixture while making it a mole ratio with acrylamide set to 3:7 might become 30 % of the weight. Moreover, the rate to the above-mentioned monomer component N and N-methylenebis acrylamide It taught so that it might become 0.1-mol %.

[0077] Next, while blowing nitrogen gas into the above-mentioned reaction mixture and driving out dissolved oxygen, nitrogen inert gas replacement of the system of reaction was carried out. Then, after carrying out the temperature up of the temperature of reaction mixture to 20 degrees C using a water bath, the 10-% of the weight sodium persulfate water-solution (radical generating agent) 4.88 as a polymerization initiator section and the 1-% of the weight sodium L-ascorbate water-solution (reducing agent) 4.81 section were added. And stirring was stopped after stirring and mixing this reaction mixture.

Then, the polymerization reaction was started immediately. Sodium persulfate was added so that the rate to a monomer component might become 0.15-mol %. Moreover, sodium L-ascorbate was added so that the rate to a monomer component might become 0.02-mol %.

[0078] In the above-mentioned polymerization reaction, 3 minutes after starting a reaction, the temperature of reaction mixture It became 108 degrees C and the peak was reached. In the meantime, the temperature up of the temperature of a water bath was suitably carried out so that it might become almost equal to the temperature of reaction mixture, until it became 90 degrees C. After the temperature of reaction mixture reached the peak, the temperature of a water bath was maintained at 80 degrees C, and this reaction mixture was riped for 30 minutes. The obtained water gel polymer was taken out after reaction termination, and it cracked in the shape of a particle.

[0079] When desiccation, grinding, etc. made the cracked water gel polymer be the same as that of an example 1, the liquid absorption agent of the magnitude of 60 meshes - 100 meshes was obtained. The liquid absorption scale factor of the obtained liquid absorption agent was 24.6 g/g. This liquid absorption agent was further ground like the example 1, and the liquid absorption agent powder whose mean particle diameter is 26 micrometers was obtained.

[0080] Next, the same actuation as an example 1 was performed using the above-mentioned liquid absorption agent powder, and water bloating tendency rubber was obtained. The bloating tendency and elution nature of water bloating tendency rubber which were obtained were measured. The result was indicated to Table 1.

[0081] [Example 8] To the same reactor as an example 1, it is a 40-% of the weight acrylic-acid magnesium water solution. The 159 sections, methoxy polyethylene-glycol methacrylate The 176.4 sections, the ion-exchange-water 59.3 section, and the polyethylene-glycol diacrylate 0.65 section were taught, and it considered as reaction mixture. The number of average addition mols of the ethyleneoxide in the above-mentioned methoxy polyethylene-glycol methacrylate is nine mols. Moreover, the number of average addition mols of the ethyleneoxide in polyethylene-glycol diacrylate is eight mols.

[0082] That is, both were taught so that the concentration of the acrylic-acid component in an acrylic-acid magnesium water solution and the monomer component in reaction mixture while making it a mole ratio with methoxy polyethylene-glycol methacrylate set to 67:33 might become 60 % of the weight. Moreover, polyethylene-glycol diacrylate was taught so that the rate to the above-mentioned monomer component might become 0.12-mol %.

[0083] Next, while blowing nitrogen gas into the above-mentioned reaction mixture and driving out dissolved oxygen, nitrogen inert gas replacement of the system of reaction was carried out. Then, 10 % of the weight after carrying out the temperature up of the temperature of reaction mixture to 50 degrees C using a water bath The 2 and 2'-azobis (2-amidinopropane) hydrochloride water-solution 4.64 section was added. And stirring was stopped after stirring and mixing this reaction mixture. Then, the polymerization reaction was started immediately. The 2 and 2'-azobis (2-amidinopropane) hydrochloride was added so that the rate to a monomer component might become 0.15-mol %.

[0084] In the above-mentioned polymerization reaction, 49 minutes after starting a reaction, the temperature of reaction mixture It became 104 degrees C and the peak was reached. In the meantime, the temperature up of the temperature of a water bath was suitably carried out so that it might become almost equal to the temperature of reaction mixture, until it became 90 degrees C. After the temperature of reaction mixture reached the peak, the temperature of a water bath was maintained at 80 degrees C, and this reaction mixture was riped for 30 minutes. The obtained water gel polymer was taken out after reaction termination, and it cracked in the shape of a particle.

[0085] When desiccation, grinding, etc. made the cracked water gel polymer be the same as that of an example 1, the liquid absorption agent of the magnitude of 60 meshes - 100 meshes was obtained. The liquid absorption scale factor of the obtained liquid absorption agent was 13.4 g/g. This liquid absorption agent was further ground like the example 1, and the liquid absorption agent powder whose mean particle diameter is 25 micrometers was obtained.

[0086] Next, the same actuation as an example 1 was performed using the above-mentioned liquid absorption agent powder, and water bloating tendency rubber was obtained. The bloating tendency and

elution nature of water bloating tendency rubber which were obtained were measured. The result was indicated to Table 1.

[0087] [Example 1 of a comparison] It is from the 0.41 sections about the amount of the polyethylene-glycol diacrylate used in an example 1. It changed into the 8.2 sections. That is, the rate to a monomer component polyethylene-glycol diacrylate Except having taught so that it might become 3.0-mol %, the same reaction and actuation as an example 1 were performed, and the liquid absorption agent for a comparison was obtained. Liquid absorption scale factor of the obtained liquid absorption agent for a comparison It was 3.8 g/g. The liquid absorption agent for this comparison was further ground like the example 1, and the liquid absorption agent powder for a comparison whose mean particle diameter is 20 micrometers was obtained.

[0088] Next, the same actuation as an example 1 was performed using the liquid absorption agent powder for the above-mentioned comparison, and the water bloating tendency rubber for a comparison was obtained. The bloating tendency and elution nature of water bloating tendency rubber for a comparison which were obtained were measured. The result was indicated to Table 1.

[0089] [Example 2 of a comparison] To the same reactor as an example 1, it is a 43-% of the weight sodium methacrylate water solution. The 178.0 sections, methoxy polyethylene-glycol methacrylate The 163.4 sections, the ion-exchange-water 53.9 section, and the polyethylene-glycol diacrylate 0.25 section were taught, and it considered as reaction mixture. The number of average addition mols of the ethyleneoxide in the above-mentioned methoxy polyethylene-glycol methacrylate is nine mols. Moreover, the number of average addition mols of the ethyleneoxide in polyethylene-glycol diacrylate is eight mols.

[0090] That is, the mole ratio of the methacrylic-acid component in a sodium methacrylate water solution and methoxy polyethylene-glycol methacrylate taught both so that it might be set to 67:33. Moreover, polyethylene-glycol diacrylate was taught so that the rate to the above-mentioned monomer component might become 0.05-mol %.

[0091] Next, while blowing nitrogen gas into the above-mentioned reaction mixture and driving out dissolved oxygen, nitrogen inert gas replacement of the system of reaction was carried out. Then, 10 % of the weight after carrying out the temperature up of the temperature of reaction mixture to 40 degrees C using a water bath 2 and 2'-azobis (2-amidinopropane) hydrochloride water solution The 4.3 sections were added. And stirring was stopped after stirring and mixing this reaction mixture. Then, the polymerization reaction was started immediately. The 2 and 2'-azobis (2-amidinopropane) hydrochloride was added so that the rate to a monomer component might become 0.15-mol %.

[0092] Since a reaction is started in the above-mentioned polymerization reaction The temperature of reaction mixture became 88 degrees C after 107 minutes, and the peak was reached. In the meantime, the temperature up of the temperature of a water bath was suitably carried out so that it might become almost equal to the temperature of reaction mixture. After the temperature of reaction mixture reached the peak, the temperature of a water bath was maintained at 80 degrees C, and this reaction mixture was riped for 60 minutes. The obtained water gel polymer was taken out after reaction termination, and it cracked in the shape of a particle.

[0093] When desiccation, grinding, etc. made the cracked water gel polymer be the same as that of an example 1, the liquid absorption agent for the comparison of the magnitude of 60 meshes - 100 meshes was obtained. The liquid absorption scale factor of the obtained liquid absorption agent for a comparison was 21.8 g/g. The liquid absorption agent for this comparison was further ground like the example 1, and the liquid absorption agent powder for a comparison whose mean particle diameter is 20 micrometers was obtained.

[0094] Next, the same actuation as an example 1 was performed using the liquid absorption agent powder for the above-mentioned comparison, and the water bloating tendency rubber for a comparison was obtained. The bloating tendency and elution nature of water bloating tendency rubber for a comparison which were obtained were measured. The result was indicated to Table 1.

[0095] [Example 3 of a comparison] To the same reactor as an example 1, it is a 37-% of the weight acrylic-acid sodium water solution. The 116.8 sections, 40-% of the weight acrylamide water solution

The 192 sections, ion-exchange-water 64.5 section and 1.5-% of the weight N, and N-methylenebis acrylamide water-solution 15.8 section was taught, and it considered as reaction mixture.

[0096] That is, both were taught so that the concentration of the acrylic-acid component in an acrylic-acid sodium water solution and the monomer component in reaction mixture while making it a mole ratio with acrylamide set to 3:7 might become 30 % of the weight. Moreover, the rate to the above-mentioned monomer component N and N-methylenebis acrylamide It taught so that it might become 0.1-mol %.

[0097] Next, while blowing nitrogen gas into the above-mentioned reaction mixture and driving out dissolved oxygen, nitrogen inert gas replacement of the system of reaction was carried out. Then, 10-% of the weight sodium persulfate water solution after carrying out the temperature up of the temperature of reaction mixture to 20 degrees C using a water bath The 5.5 sections and the 1-% of the weight sodium L-ascorbate water-solution 5.42 section were added. And stirring was stopped after stirring and mixing this reaction mixture. Then, the polymerization reaction was started immediately. Sodium persulfate was added so that the rate to a monomer component might become 0.15-mol %. Moreover, sodium L-ascorbate was added so that the rate to a monomer component might become 0.02-mol %.

[0098] In the above-mentioned polymerization reaction, 17 minutes after starting a reaction, the temperature of reaction mixture It became 108 degrees C and the peak was reached. In the meantime, the temperature up of the temperature of a water bath was suitably carried out so that it might become almost equal to the temperature of reaction mixture, until it became 90 degrees C. After the temperature of reaction mixture reached the peak, the temperature of a water bath was maintained at 80 degrees C, and this reaction mixture was riped for 30 minutes. The obtained water gel polymer was taken out after reaction termination, and it cracked in the shape of a particle.

[0099] When desiccation, grinding, etc. made the cracked water gel polymer be the same as that of an example 1, the liquid absorption agent for the comparison of the magnitude of 60 meshes - 100 meshes was obtained. The liquid absorption scale factor of the obtained liquid absorption agent for a comparison was 21.7 g/g. The liquid absorption agent for this comparison was further ground like the example 1, and the liquid absorption agent powder for a comparison whose mean particle diameter is 19 micrometers was obtained.

[0100] Next, the same actuation as an example 1 was performed using the liquid absorption agent powder for the above-mentioned comparison, and the water bloating tendency rubber for a comparison was obtained. The bloating tendency and elution nature of water bloating tendency rubber for a comparison which were obtained were measured. The result was indicated to Table 1.

[0101] [Example 4 of a comparison] It replaced with the liquid absorption agent powder 50 section in an example 1, and except having used the absorptivity resin (NIPPON SHOKUBAI Make; trade name AKUA rucksack K-4) 50 section of a commercial sodium polyacrylate system, the same actuation as an example 1 was performed, and the water bloating tendency rubber for a comparison was obtained. The bloating tendency and elution nature of water bloating tendency rubber for a comparison which were obtained were measured. The result was indicated to Table 1.

[0102]

[Table 1]

		吸液剤の 吸液倍率 (g/g)	水 膨 潤 性 ゴ ム の 性 能			
			膨 潤 性			溶 出 性
			膨潤倍率 (倍)		膨潤 倍率比	過マンガン酸 カリウムの消 費量 (mg/l)
			水道水	人工海水		
実 施 例	1	20.8	3.2	3.0	0.94	1.6
	2	23.3	3.3	3.0	0.91	1.8
	3	18.3	3.3	2.9	0.88	2.2
	4	5.5	2.4	2.2	0.92	1.6
	5	51.3	4.6	3.6	0.78	4.4
	6	22.4	3.3	2.8	0.85	3.8
	7	24.6	2.9	2.5	0.86	3.3
	8	13.4	2.6	2.4	0.92	2.8
比 較 例	1	3.8	1.8	1.7	0.94	1.6
	2	21.8	4.1	2.6	0.63	5.3
	3	21.7	3.7	2.5	0.68	6.3
	4	—	3.1	1.4	0.45	10.8

[0103] It is both twice [more than] the swelling scale factor when absorbing the swelling scale factor when absorbing tap water, and artificial sea water of this, and the water bloating tendency rubber concerning this example has a swelling scale-factor ratio close to 1 so that clearly from Table 1. On the other hand, since the liquid absorption scale factor of a liquid absorption agent is under 5 g/g, both the swelling scale factors of the water bloating tendency rubber for the comparison of the example 1 of a comparison are under 2 double. Moreover, the water bloating tendency rubber for the comparison of the example 2 of a comparison - the example 4 of a comparison has a swelling scale-factor ratio extremely smaller than 1. Furthermore, this consumption of the water bloating tendency rubber for the comparison of the example 2 of a comparison - the example 4 of a comparison is 5mg/l. or more to the consumption of potassium permanganate of the water bloating tendency rubber concerning this example being less than 5 mg/l.

[0104] That is, it turns out that the water bloating tendency rubber concerning this example does not almost have the difference of both the swelling scale factor while it is excellent in the swelling scale factor when absorbing the swelling scale factor when absorbing tap water, and artificial sea water, and the leached moiety (melttable component) is moreover reduced rather than the water bloating tendency rubber for a comparison so that clearly from the result of an example 1 - an example 8, and the example 1 of a comparison - the example 4 of a comparison.

[Translation done.]

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